

TITLE OF THE INVENTION

SILVER HALIDE PHOTOGRAPHIC LIGHTSENSITIVE MATERIAL

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is based upon and claims the  
5 benefit of priority from the prior Japanese Patent  
Applications No. 2001-000800, filed January 5, 2001;  
and No. 2001-374801, filed December 7, 2001, the entire  
contents of both of which are incorporated herein by  
reference.

10 BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a silver halide  
photographic lightsensitive material. More  
specifically, the present invention relates to a highly  
15 sensitive, low-fogging silver halide photographic  
lightsensitive material.

2. Description of the Related Art

A silver halide photographic lightsensitive  
material mainly comprises a dispersion medium  
20 containing lightsensitive silver halide grains applied  
on a support. To increase the sensitivity of silver  
halide lightsensitive materials, an enormous amount of  
study has been made. In order to enhance the  
sensitivity of a silver halide lightsensitive material,  
25 it is very important to increase the sensitivity  
inherent to the silver halide grains. For increasing  
the sensitivity of silver halide grains, various

methods are employed. Enhancement of sensitivity are accomplished, such as enhancement of sensitivity using chemical sensitizers such as sulfur, gold and compounds of the VIII Group; enhancement of sensitivity using a combination of chemical sensitizers such as sulfur, gold and compounds of the VIII Group, and additives that facilitate the sensitizing effect of the chemical sensitizers; and enhancement of sensitivity by the addition of an additive having an sensitizing effect depending on a kind of silver halide emulsion. Descriptions on these methods can be found in Research Disclosure, Vol. 120, April, 1974, 12008, Research Disclosure, Vol. 34, June, 1975, 13452, U.S.P. Nos. 2,642,361, 3,297,446, 3,772,031, 3,857,711, 3,901,714, 4,266,018 and 3,904,415, and British Patent No. 1,315,755. Further, a method comprising reduction-sensitizing silver halide grains is also employed as a method for enhancing sensitivity. Reduction-sensitization of silver halide grains is disclosed in, for example, U.S.P Nos. 2,518,698, 3,201,254, 3,411,917, 3,779,777 and 3,930,867, and a method of using a reducing agent is disclosed in, for example, Jpn. Pat. Appln. KOKOKU Publication No. (hereinafter referred to as JP-B-) 57-33572, JP-B-58-1410, and Jpn. Pat. Appln. KOKAI Publication No. (hereinafter referred to as JP-A-) 57-179835. Furthermore, a sensitizing technique using an organic electron-donating compound comprising

an electron-donating group and a leaving group has been reported as described recently in U.S.P. Nos. 5747235 and 5747236, EP Nos. 786692A1, 893731A1 and 893732A1, and WO99/05570. This is a novel sensitizing technique and is effective in enhancement of sensitivity.

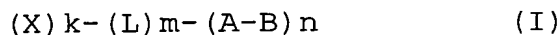
However, although the use of this compound results in an enhanced sensitivity, it has also the defect that the fogging or Dmin becomes high, and therefore improvement has been desired.

#### BRIEF SUMMARY OF THE INVENTION

The present invention was accomplished in order to solve the problems with the above-mentioned conventional techniques, and it is an object of the invention to provide a highly sensitive, low-fogging silver halide photographic lightsensitive material.

The object of the present invention has successfully been attained by the following approaches:

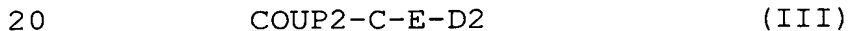
(1) A silver halide photographic lightsensitive material comprising a support having thereon at least one lightsensitive silver halide emulsion layer, wherein the lightsensitive material contains at least one compound represented by general formula (I) and at least one photographically useful group-releasing compound represented by general formula (II) or (III) that is capable of forming a compound having substantially no contribution to a dye after its coupling with an oxidized form of a developing agent:



wherein X represents an adsorbing group to silver halide or a light-absorbing group having at least one atom selected from the group consisting of N, S, P, Se and Te; L represents a bivalent linking group having at least one atom selected from the group consisting of C, N, S and O; A represents an electron-donating group; B represents a leaving group or a hydrogen atom, wherein after  $-(A-B)_n$  portion is oxidized, B is eliminated or deprotonated thereby to form a radical  $A\cdot$ ; k and m independently represent an integer of 0 to 3; and n represents 1 or 2;



wherein COUP1 represents a coupler residue capable of releasing D1 by a coupling reaction with an oxidized form of a developing agent, along with forming a water-soluble or alkali-soluble compound; and D1 represents a photographically useful group or its precursor which is bonded to the coupling position of COUP1;

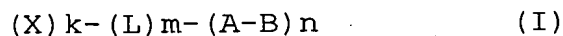


wherein COUP2 represents a coupler residue capable of coupling with an oxidized form of a developing agent; E represents an electrophilic portion; C represents a single bond or a bivalent linking group capable of releasing D2, along with a 4- to 8-membered ring formation, through an intramolecular nucleophilic substitution reaction between the electrophilic portion



E and a nitrogen atom, wherein the nitrogen atom originates from the developing agent and is bonded to the coupling position in a coupling product between COUP2 and the oxidized form of the developing agent, and wherein C may be bonded to COUP2 at the coupling position of COUP2 or may be bonded to COUP2 at a position other than the coupling position of COUP2; and D2 represents a photographically useful group or its precursor.

(2) A silver halide photographic lightsensitive material comprising a support having thereon at least one lightsensitive silver halide emulsion layer containing an emulsified dispersion, wherein the lightsensitive material contains at least one compound represented by general formula (I), and the emulsified dispersion contains at least one surfactant having a critical micelle concentration of  $4.0 \times 10^{-3}$  mol/L or less in an amount of 0.01% by weight or more based on all the ingredients in the lightsensitive layer where the surfactant is contained:

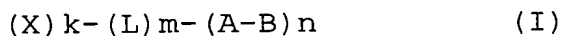


wherein X represents an adsorbing group to silver halide or a light-absorbing group having at least one atom selected from the group consisting of N, S, P, Se and Te; L represents a bivalent linking group having at least one atom selected from the group consisting of C, N, S and O; A represents an electron-donating group; B

represents a leaving group or a hydrogen atom, wherein after  $-(A-B)_n$  portion is oxidized, B is eliminated or deprotonated thereby to form a radical  $A\cdot$ ; k and m independently represent an integer of 0 to 3; and n represents 1 or 2.

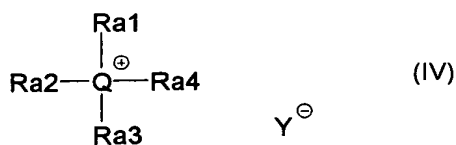
(3) The silver halide lightsensitive material according to item (1) above, wherein the emulsified dispersion further contains a high-boiling organic solvent having a dielectric constant of 7.0 or less.

(4) A silver halide photographic lightsensitive material comprising a support having thereon at least one lightsensitive silver halide emulsion layer, wherein the lightsensitive material contains at least one compound represented by general formula (I), and the silver halide emulsion layer contains a sensitizing dye and at least one compound represented by general formula (IV) in an amount of 1 to 50 mol% or less of the sensitizing dye:



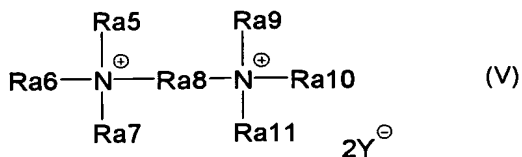
wherein X represents an adsorbing group to silver halide or a light-absorbing group having at least one atom selected from the group consisting of N, S, P, Se and Te; L represents a bivalent linking group having at least one atom selected from the group consisting of C, N, S and O; A represents an electron-donating group; B represents a leaving group or a hydrogen atom, wherein after  $-(A-B)_n$  portion is oxidized, B is eliminated or

deprotonated thereby to form a radical A<sup>•</sup>; k and m independently represent an integer of 0 to 3; and n represents 1 or 2;



wherein Q represents an N or P atom; each of Ra1, Ra2, Ra3 and Ra4 represents an alkyl group, an aryl group or a heterocyclic group, wherein two of Ra1, Ra2, Ra3 and Ra4 may be bonded with each other to thereby form a saturated ring or three of Ra1, Ra2, Ra3 and Ra4 may cooperate with each other to thereby form an unsaturated ring; and Y represents an anionic group, provided that Y does not exist in the event of an intramolecular salt.

(5) The silver halide lightsensitive material according to item (4) above, wherein the compound represented by the general formula (IV) is represented by general formula (V):



wherein each of Ra5, Ra6 and Ra7 represents an alkyl group, an aryl group or a heterocyclic group, wherein two of Ra5, Ra6 and Ra7 may cooperate with each other to thereby form a saturated ring, or three of Ra5, Ra6 and Ra7 may cooperate with each other to thereby form an unsaturated ring; Ra8 represents a divalent

group constituted by each or any combination of an alkylene group, an arylene group, -O-, -S- and -CO<sub>2</sub>-, provided that each of -O-, -S- and -CO<sub>2</sub>- is bonded so as to be adjacent to the alkylene group or the arylene group; Ra9, Ra10 and Ra11 each have the same meanings as Ra5, Ra6 and Ra7; and Y has the same meaning as Y of the general formula (IV).

(6) The silver halide photographic lightsensitive material according to any of items (1) to (5) above, wherein 50% or more of the total projected area of all the silver halide grains contained in the light-sensitive layer is occupied by silver halide grains satisfying the following requirements (a) to (d):

- (a) parallel main planes thereof are (111) faces,
- (b) an aspect ratio thereof is 2 or more,
- (c) ten or more dislocation lines per grain are present, and

(d) tabular silver halide grains each formed of silver iodobromide or silver chloriodobromide whose silver chloride content is less than 10 mol%

(7) The silver halide photographic lightsensitive material according to any one of items (1) to (5) above, wherein 50% or more of the total projected area of all the silver halide grains contained in the lightsensitive layer is occupied by silver halide grains satisfying the following requirements (a), (d) and (e):

(a) parallel main planes thereof are (111) faces,

(d) tabular silver halide grains each formed of silver iodobromide or silver chloriodobromide whose silver chloride content is less than 10 mol%, and

5 (e) hexagonal tabular grains each having at least one epitaxial junction per grain at an apex portion and/or a side face portion and/or a main plane portion thereof

(8) The silver halide photographic lightsensitive  
10 material according to any one of items (1) to (5) above, wherein 50% or more of the total projected area of all the silver halide grains contained in the lightsensitive layer is occupied by silver halide grains satisfying the following requirements (d), (f)  
15 and (g):

(d) tabular silver halide grains each formed of silver iodobromide or silver chloriodobromide whose silver chloride content is less than 10 mol%,

(f) parallel main planes thereof are (100) faces,  
20 and

(g) an aspect ratio thereof is 2 or more

(9) The silver halide photographic lightsensitive material according to any of items (1) to (5) above, wherein 50% or more of the total projected area of all  
25 the silver halide grains contained in the lightsensitive layer is occupied by silver halide grains satisfying the following requirements (g), (h)

and (i):

(g) an aspect ratio thereof is 2 or more,

(h) parallel main planes thereof are (111) faces or (100) faces, and

5 (i) tabular grains each having a silver chloride content of at least 80 mol%

(10) The silver halide photographic  
lightsensitive material according to any one of items  
(6) to (9) above, wherein the silver halide grains  
10 accounting for 50% or more of the total projected area  
of all the silver halide grains contained in the  
lightsensitive layer further satisfying the following  
requirements (j), (k) and (m):

(j) a projected area diameter thereof is 2  $\mu\text{m}$  or  
15 more,

(k) an aspect ratio thereof is 10 or more, and

(m) an average AgI content of the individual  
grains is 5 mol% or more

(11) The silver halide photographic  
20 lightsensitive material according to item (6) or (7)  
above, wherein the silver halide grains accounting for  
the 50% or more of the total projected area of all the  
silver halide grains contained in the lightsensitive  
layer further satisfying the following requirement (j);  
25 and 80% or more of the total projected area of all the  
silver halide grains contained in the lightsensitive  
layer is occupied by silver halide grains each having

no dislocation line in the region within 50% from the center of the grain projected area thereof:

(j) a projected area diameter thereof is 2  $\mu\text{m}$  or more

5           (12) The silver halide photographic  
lightsensitive material according to item (6) above,  
wherein the silver halide grains accounting for 50% or  
more of the total projected area of all the silver  
halide grains contained in the lightsensitive layer,  
10       are those prepared by a production method comprising,  
during formation of grains, a step of forming grains  
while rapidly generating an iodide ion using an iodide  
ion-releasing agent.

15           (13) The silver halide photographic  
lightsensitive material according to item (6) above,  
wherein the silver halide grains accounting for 50% or  
more of the total projected area of all the silver  
halide grains contained in the lightsensitive layer,  
are those prepared by a production method comprising,  
20       during formation of grains, a step of adding silver  
iodide fine grains to a vessel in which the formation  
of grains is being performed.

25           (14) The silver halide photographic  
lightsensitive material according to item (13) above,  
wherein the silver iodide fine grains are those formed  
outside the vessel in which the formation of grains is  
being performed.

(15) The silver halide photographic  
lightsensitive material according to any one of items  
(6) to (9) above, wherein at least 30% of the total  
silver amount of the silver halide grains that are  
5 accounting for 50% or more of the total projected area  
of the silver halide grains contained in the  
lightsensitive layer, are prepared by a method  
comprising, during formation of grains, a step of  
adding, to a vessel in which the formation of grains is  
10 performed, silver halide fine grains formed in another  
vessel.

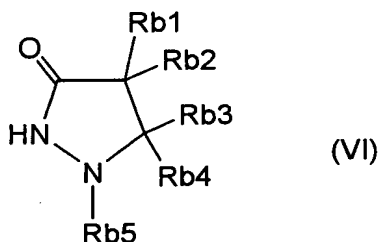
(16) The silver halide photographic  
lightsensitive material according to any one of items  
(6) to (15) above, wherein the silver halide grains  
15 accounting for the 50% or more of the total projected  
area of all the silver halide grains contained in the  
lightsensitive layer, are those subjected to a  
reduction-sensitization.

(17) The silver halide photographic  
20 lightsensitive material according to any one of items  
(6) to (16) above, wherein the silver halide emulsion  
contained in the lightsensitive layer, contains gelatin  
comprising components, in an amount of 20% or more,  
each having a molecular weight of 280,000 or more.

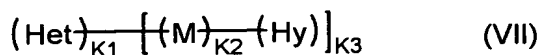
25 (18) The silver halide photographic  
lightsensitive material according to any one of items  
(1) to (17), wherein the lightsensitive layer contains



at least one of compounds represented by general formulas (VI), (VII), (VIII-1), (VIII-2), (IX-1), (IX-2), (X) and (XI):

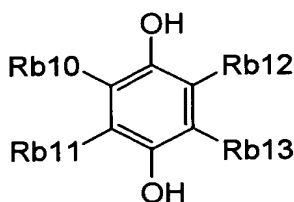


wherein Rb1, Rb2, Rb3 and Rb4 each independently represent a hydrogen atom, an aryl group, a chain-like or cyclic alkyl group, a chain-like or cyclic alkenyl group or an alkynyl group; and Rb5 represents a chain-like or cyclic alkyl group, a chain-like or cyclic alkenyl group, an alkynyl group, an aryl group or a heterocyclic group;

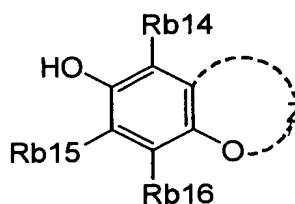


wherein Het is an adsorbing group to silver halide; M represents a bivalent linking group comprising an atom or atomic group containing at least one of a carbon atom, a nitrogen atom, a sulfur atom and an oxygen atom; Hy represents a group having a hydrazine structure represented by Rb6Rb7N-NRb8Rb9, wherein Rb6, Rb7, Rb8 and Rb9 each independently represent an alkyl group, an alkenyl group, an alkynyl group, an aryl group or a heterocyclic group, and Rb6 and Rb7, Rb8 and Rb9, Rb6 and Rb8, or Rb7 and Rb9 may be bonded together to form a ring, provided that at

least one of Rb6, Rb7, Rb8 and Rb9 is an alkylene group,  
 an alkenylene group, an alkynylene group, an arylene  
 group or a bivalent heterocyclic residue for being  
 substituted with  $-(M)k_2(Het)k_1$  in the general formula  
 5 (VII);  $k_1$  and  $k_3$  each independently represent 1, 2, 3  
 or 4; and  $k_2$  represents 0 or 1;



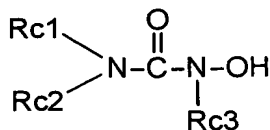
(VIII-1)



(VIII-2)

10 in formula (VIII-1), Rb10, Rb11, Rb12 and Rb13  
 each independently represent a hydrogen atom or a  
 substituent, provided that when Rb10 and Rb13 each are  
 an alkyl group, or Rb11 and Rb12 each are an alkyl  
 group, these are not substituents having the same  
 number of carbon atoms; and

15 in formula (VIII-2), Rb14, Rb15 and Rb16 each  
 independently represent a hydrogen atom or a  
 substituent, and Z represents a non-metallic atomic  
 group forming a 4- to 6-membered ring;



(IX-1)

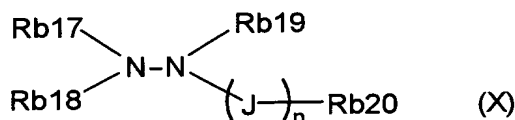
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wherein Rc1 represents a substituted or  
 unsubstituted alkyl, a substituted or unsubstituted  
 alkenyl or a substituted or unsubstituted aryl group;  
 Rc2 represents a hydrogen atom or the same groups as

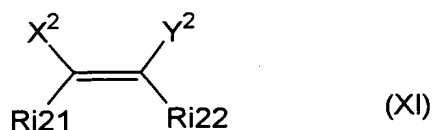
those represented by R<sub>c1</sub>; and R<sub>c3</sub> represented by a hydrogen atom or a substituted or unsubstituted alkyl or a substituted or unsubstituted alkenyl group having 1 to 10 carbon atoms, wherein R<sub>c1</sub> and R<sub>c2</sub>, R<sub>c1</sub> and R<sub>c3</sub>, or R<sub>c2</sub> and R<sub>c3</sub> may be bonded together to form a 5- to 7-membered ring;



wherein each of G1 and G2 represents a hydrogen atom or a monovalent substituent, provided that these may be bonded together to form a ring;



wherein Rb17, Rb18 and Rb19 each independently represent a hydrogen atom, an alkyl group, an alkenyl group, an aryl group or a heterocyclic group; Rb20 represents a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group, an aryl group, a heterocyclic group or -NRb21Rb22, wherein Rb21 represents a hydrogen atom, a hydroxyl group, an amino group, an alkyl group, an alkenyl group, an alkynyl group, an aryl group or a heterocyclic group, and Rb22 represents a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group, an aryl group or a heterocyclic group; J represents -CO- or -SO<sub>2</sub>-; and n represents 0 or 1; wherein Rb17 and Rb18, Rb17 and Rb19, Rb19 and Rb20, or Rb20 and Rb18 may be bonded together to form a ring;



wherein  $\text{X}^2$  and  $\text{Y}^2$  each independently represent a hydroxyl group,  $-\text{NRi23Ri24}$  or  $-\text{NHSO}_2\text{Ri25}$ ; and Ri21 and  
5 Ri22 each independently represent a hydrogen atom or an optional substituent, wherein Ri21 and Ri22 may be bonded together to form a carbon ring or a heterocycle; Ri23 and Ri24 each independently represent a hydrogen  
10 atom, an alkyl group, an aryl group or a heterocyclic group, wherein Ri23 and Ri24 may be bonded together to form a heterocycle; and Ri25 represents an alkyl group, an aryl group, an amino group or a heterocyclic group.

Additional objects and advantages of the invention will be set forth in the description which follows, and  
15 in part will be obvious from the description, or may be learned by practice of the invention. The objects and advantages of the invention may be realized and obtained by means of the instrumentalities and combinations particularly pointed out hereinafter.

#### 20 DETAILED DESCRIPTION OF THE INVENTION

The present invention will be described in detail below.

A silver halide emulsion in the present invention preferably is silver bromide, silver chloride, silver  
25 iodobromide, silver iodochlorobromide, silver chlorobromide, silver chloriodobromide, and the like. The form of the silver halide grain may be a normal

crystal such as octahedron, cube and tetradecahedron, but a tabular grain is preferable.

First, a description will be made to a first emulsion relative to the present invention, that is, 5 tabular silver halide grains each comprising silver iodobromide or silver chloriodobromide whose silver chloride content is less than 10 mol%, and each having (111) faces as its parallel main planes.

This emulsion comprises opposing (111) main planes 10 and side faces connecting the main planes. A tabular grain emulsion is formed of silver iodobromide or silver chloriodobromide. The emulsion may contain silver chloride, but the silver chloride content is preferably 8 mol% or less, more preferably 3 mol% or less or 0 mol%. The silver iodide content is 0.5 mol% 15 or more and 40 mol% or less, and preferably 1.0 mol% or more and 20 mol% or less.

Regardless of the silver iodide content, the variation coefficient of intergrain distribution of 20 silver iodide content is preferably 20% or less, and particularly preferably 10% or less.

With respect to the silver iodide distribution, it is preferable that the grains have a structure within the grains. In such as case, it is possible for the 25 structure of silver iodide distribution to be a double, triple, quadruple, quintuple, or more multiple structures. The silver iodide content may be changed

continuously within a grain.

Grains having an aspect ratio of 2 or more occupy 50% or more of the total projected area. The projected area and aspect ratio of the tabular grains can be measured from an electron micrograph according to the technique of carbon replica shadowed together with spherical latex particles for reference. The tabular grains, when viewed from above its main planes, generally have a hexagonal, triangular or circular shape, and the aspect ratio is a quotient obtained by dividing the diameter of a circle having an area equal to the projected area of a grain by the thickness thereof. The higher the ratio of hexagons is, the more preferable the shape of the tabular grains. Further, the ratio of lengths of mutually neighboring sides of the hexagon is preferably 1:2 or less.

The tabular grains preferably have a size of 0.1  $\mu\text{m}$  or more and 20.0  $\mu\text{m}$  or less, and more preferably 0.2  $\mu\text{m}$  or more and 10.0  $\mu\text{m}$  or less, in terms of the projected area diameter. The "projected area diameter" of a silver halide grain refers to a diameter of a circle having an area equal to the projected area of the silver halide grain. The thickness of the tabular grains preferably is 0.01  $\mu\text{m}$  or more and 0.5  $\mu\text{m}$  or less, and more preferably 0.02  $\mu\text{m}$  or more and 0.4  $\mu\text{m}$  or less. The thickness of a tabular grain refers to the distance between two main planes. The tabular grains preferably

have a size of 0.1  $\mu\text{m}$  or more and 5.0  $\mu\text{m}$  or less, and more preferably from 0.2  $\mu\text{m}$  or more and 3  $\mu\text{m}$  or less, in terms of the equivalent-sphere diameter. The "equivalent-sphere diameter" of a grain refers to a diameter of a sphere having a volume equal to the volume of individual grains. Further, the aspect ratio is preferably 1 or more and 100 or less, and more preferably 2 or more and 50 or less. The aspect ratio of a grain refers to a quotient obtained by dividing the diameter of a circle having an area equal to the projected area of the grain by the thickness thereof.

The silver halide grains contained in the first emulsion and the second emulsion used in the present invention are preferably monodisperse. The variation coefficient of sphere equivalent diameter of all the silver halide grains contained in the first and second emulsions related to the present invention is 30% or less, and preferably 25% or less. Further, in the case of tabular grains, the variation coefficient of projected area diameter is also important. The variation coefficient of projected area diameter of all the silver halide grains contained in the first and second emulsions related to the present invention is preferably 30% or less, more preferably 25% or less, and still more preferably 20% or less. Furthermore, the variation coefficient of thickness of the tabular grains is preferably 30% or less, more preferably 25%

or less, and still more preferably 20% or less. The variation coefficient of projected area diameter of silver halide grains refers to a quotient obtained by dividing the standard deviation of the projected area diameter distribution of the individual silver halide grains by the average equivalent-circle diameter thereof. The variation coefficient of thickness of tabular silver halide grains refers to a quotient obtained by dividing the standard deviation of the thickness distribution of the individual tabular silver halide grains by the average thickness thereof.

The distance between twin planes of the tabular grains contained in the first and second emulsions related to the present invention may be set to  $0.012\text{ }\mu\text{m}$  or less as disclosed in U.S.P. No. 5,219,720. Alternatively, the ratio of the distance between (111) main planes to the distance between twin planes may be set to 15 or more as disclosed in JP-A-5-249585. A selection suitable to application may be made.

The greater the aspect ratio is, the more conspicuous the effect attained. Thus, it is preferable that grains having an aspect ratio of 5 or more, more preferably 8 or more, occupy 50% or more of the total projected area of the tabular grain emulsion. Too great aspect ratios tend to increase the above-mentioned variation coefficient of grain size distribution. Thus, it is generally preferred that the



aspect ratio is 100 or less.

The dislocation lines of the tabular grains can be observed by the direct method using a transmission electron microscope at low temperatures as described in, for example, J. F. Hamilton, Phot. Sci. Eng., 11, 57 (1967) and T. Shiozawa, J. Soc. Phot. Sci. Japan, 3, 5, 213 (1972). Illustratively, silver halide grains are harvested from the emulsion with the care that the grains are not pressurized with such a force that dislocation lines occur on the grains, are put on a mesh for electron microscope observation and, while cooling the specimen so as to prevent damaging (printout, etc.) by electron beams, are observed by the transmission method. The greater the thickness of the above grains, the more difficult the transmission of electron beams. Therefore, the use of an electron microscope of high voltage type (at least 200 kV on the grains of 0.25  $\mu\text{m}$  in thickness) is preferred for ensuring clearer observation. The thus obtained photograph of grains enables determining the position and number of dislocation lines in each grain viewed in the direction perpendicular to the principal planes.

The number of dislocation lines of the tabular grains according to the present invention is preferably at least 10 per grain on the average and more preferably at least 20 per grain on the average. When dislocation lines are densely present or when

dislocation lines are observed in the state of crossing each other, it happens that the number of dislocation lines per grain cannot accurately be counted. However, in this instance as well, rough counting on the order of, for example, 10, 20 or 30 dislocation lines can be effected, so that a clear distinction can be made from the presence of only a few dislocation lines. The average number of dislocation lines per grain is determined by counting the number of dislocation lines of each of at least 100 grains and calculating a number average thereof. There are instances when hundreds of dislocation lines are observed.

Dislocation lines can be introduced in, for example, the vicinity of the side faces of tabular grains. In this instance, the dislocation is nearly perpendicular to the side faces, and each dislocation line extends from a position corresponding to  $x\%$  of the distance between the center of tabular grains and the side (periphery), to the side faces. The value of  $x$  preferably ranges from 10 to less than 100, more preferably from 30 to less than 99, and most preferably from 50 to less than 98. In this instance, the figure created by binding the positions from which the dislocation lines start is nearly similar to the configuration of the grain. The created figure may be one that is not a complete similar figure but deviated. The dislocation lines of this type

are not observed around the center of the grain. The dislocation lines are crystallographically oriented approximately in the (211) direction. However, the dislocation lines often meander and may also cross each other.

Dislocation lines may be positioned either nearly uniformly over the entire zone of the periphery of the tabular grains or local points of the periphery. That is, referring to, for example, hexagonal tabular silver halide grains, dislocation lines may be localized either only in the vicinity of six apexes or only in the vicinity of one of the apexes. Contrarily, dislocation lines can be localized only in the sides excluding the vicinity of six apexes.

Furthermore, dislocation lines may be formed over regions including the centers of two mutually parallel principal planes of tabular grains. In the case where dislocation lines are formed over the entire regions of the principal planes, the dislocation lines may crystallographically be oriented approximately in the (211) direction when viewed in the direction perpendicular to the principal planes, and the formation of the dislocation lines may be effected either in the (110) direction or randomly. Further, the length of each dislocation line may be random, and the dislocation lines may be observed as short lines on the principal planes or as long lines extending to the

side (periphery). The dislocation lines may be straight or often meander. In many instances, the dislocation lines cross each other.

The position of dislocation lines may be localized on the periphery, principal planes or local points as mentioned above, or the formation of dislocation lines may be effected on a combination thereof. That is, dislocation lines may be concurrently present on both the periphery and the principal planes.

The silver iodide content on the grain surface of a tabular grain emulsion of the present invention is preferably 10 mol% or less, and particularly preferably, 5 mol% or less. The silver iodide content on the grain surface of the present invention is measured by using XPS (X-ray Photoelectron Spectroscopy). The principle of XPS used in an analysis of the silver iodide content near the surface of a silver halide grain is described in Junnich Aihara et al., "Spectra of Electrons"

(Kyoritsu Library 16: issued Showa 53 by Kyoritsu Shuppan). A standard measurement method of XPS is to use Mg-K $\alpha$  as excitation X-rays and measure the intensities of photoelectrons (usually I-3d $_{5/2}$  and Ag-3d $_{5/2}$ ) of iodine (I) and silver (Ag) released from silver halide grains in an appropriate sample form.

The content of iodine can be calculated from a calibration curve of the photoelectron intensity ratio (intensity (I)/intensity (Ag)) of iodine (I) to silver

(Ag) formed by using several different standard samples having known iodine contents. XPS measurement for a silver halide emulsion must be performed after gelatin adsorbed by the surface of a silver halide grain is decomposed and removed by, e.g., proteinase. A tabular grain emulsion in which the silver iodide content on the grain surface is 10 mol% or less is an emulsion whose silver iodide content is 10 mol% or less when the emulsion grains are analyzed by XPS. If obviously two or more types of emulsions are mixed, appropriate preprocessing such as centrifugal separation or filtration must be performed before one type of emulsion is analyzed.

The structure of a tabular grain emulsion of the present invention is preferably a triple structure of silver bromide/silver iodobromide/silver bromide or a higher-order structure. The boundary of silver iodide content between structures can be either a clear boundary or a continuously gradually changing boundary. Commonly, when measured by using a powder X-ray diffraction method, the silver iodide content does not show any two distinct peaks; it shows an X-ray diffraction profile whose tail extends in the direction of high silver iodide content.

The interior silver iodide content is preferably higher than the surface silver iodide content. The interior silver iodide content is higher than the

surface silver iodide content by 3 mol% or more,  
preferably by 5 mol% or more.

Next, a description will be made to the second  
emulsion related to the present invention, that is,  
5 grains having (111) faces as their parallel main planes  
wherein there is at least one epitaxial junction per  
grain at an apex portion and/or a side face portion  
and/or a main plane portion of a hexagonal silver  
halide grain, and wherein a ratio of the length of an  
10 edge having the maximum length to the length of an edge  
having the minimum length, is 2 or less. The grain  
with an epitaxial junction refers to a grain having  
main body of the silver halide grain to which a crystal  
portion (that is, an epitaxial portion) is joined,  
15 wherein the joined crystal portion usually projects  
from the main body of the silver halide grain. It is  
preferable that the ratio of the joined crystal portion  
(epitaxial portion) to the amount of the total silver  
contained in the grain is 1% or more and 30% or less,  
20 and more preferably or more 2% and 15% or less. The  
epitaxial portion may be located anywhere in the main  
body of the grain, but it is preferably located at a  
grain main plane portion and/or a grain side face  
portion and/or a grain apex portion. The number of the  
25 epitaxial portion is preferably at least one. The  
composition of the epitaxial portion is preferably AgBr,  
AgCl, AgBrCl, AgBrClI, AgBrI, AgI, AgSCN and the like.

When there is an epitaxial portion, a dislocation line may be present inside the grain, but it does not have to be present. Further, a dislocation line does not have to be present in an epitaxial portion, a junction portion between a main portion of a silver halide grain and a junction portion, or an epitaxial portion, but it is preferable that a dislocation line is present.

Next, a description will be made to methods for preparing the first emulsion and the second emulsion silver halide grains.

The preparation process of the present invention comprises (a) a base grain forming process and a grain forming process (process (b)) following step (a). Basically, it is preferable that process (a) is followed by process (b), but only process (a) may be carried out. Process (b) may be any of (b1) a step of introducing dislocation, (b2) a step of introducing dislocation at a corner portion restrictedly, and (b3) an epitaxial junction step. Process (b) may contain either one step or a combination of two or more steps.

First, (a) base grain forming process will be described. A base portion is preferably at least 50%, more preferably 60% or more of the amount of the total silver used for the grain formation. The average content of iodine relative to the amount of silver in the base portion is preferably 0 mol% or more and 30 mol% or less, and more preferably 0 mol% or more and 15

mol% or less. The base portion may have a core-shell structure, as needed. In this case, the core portion of the base portion is preferably 50% or more and 70% or less of the amount of the total silver contained in the base portion. The average iodine composition of the core portion is preferably 0 mol% or more and 30 mol% or less, and more preferably 0 mol% or more and 15 mol% or less. The iodine composition of the shell portion is preferably 0 mol% or more and 3 mol% or less.

A method comprising forming silver halide nuclei and then allowing the silver halide grains to grow, thereby obtaining grains with a desired size is general as a method for preparing a silver halide emulsion. The present invention is certainly similar to that. Further, with respect to the formation of tabular grains, steps of, at least, nucleation, ripening and growing are contained. These steps will be described in U.S.P. No. 4,945,037 in detail. Hereafter, the steps, nucleation, ripening and growing, will be described.

#### 1. Nucleation step

The nucleation of tabular grains is in general carried out by a double jet method comprising adding a silver salt aqueous solution and an alkali halide aqueous solution to a reaction vessel containing a protective colloid aqueous solution, or a single jet method comprising adding a silver salt aqueous solution



to a protective colloid solution containing alkali halide. If necessary, a method comprising adding an alkali halide aqueous solution to a protective colloid solution containing silver salt may be used. Further, 5 if necessary, a method comprising adding a protective colloid solution, a silver salt solution and an alkali halide aqueous solution to the mixer disclosed in JP-A-2-44335, and immediately transfer the mixture to a reaction vessel may be used for the nucleation of 10 tabular grains. Further, as disclosed in U.S.P. No. 5,104,786, nucleation can be performed by passing an aqueous solution containing alkali halide and a protective colloid solution through a pipe and adding a silver salt aqueous solution thereto.

15           Gelatin is used as protective colloid but natural high polymers besides gelatin and synthetic high polymers can also be used. Alkali-processed gelatin, oxidized gelatin, i.e., gelatin in which a methionine group in the gelatin molecule is oxidized with hydrogen 20 peroxide, etc. (a methionine content of 40  $\mu\text{mol/g}$  or less), amino group-modified gelatin of the present invention (e.g., phthalated gelatin, trimellitated gelatin, succinated gelatin, maleated gelatin, and esterified gelatin), and low molecular weight gelatin 25 (molecular weight of from 3,000 to 40,000) are used. JP-B-5-12696 can be referred to about oxidized gelatin. Descriptions of JP-A's-8-82883 and 11-143002 can be

referred to about amino group-modified gelatin.

Further, if necessary, lime-processed ossein gelatin containing 20% or more, preferably 30% or more of

components having a molecular weight of 280,000 in a

5 molecular weight distribution determined by the Puggy's method disclosed in JP-A-11-237704 may be employed.

Furthermore, for example, starches disclosed in EP No. 758758 and U.S.P. No. 5,733,718 may also be used.

10 Further, natural high polymers will be described in JP-B-7-111550 and Research Disclosure, Vol. 176, No. 17643, item IX (December, 1978).

Excessive halides in the nucleation are preferably  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ , and they can be present individually or in combination. The concentration of the total  
15 halides is  $3 \times 10^{-5}$  mol/L or more and 0.1 mol/L or less, and preferably  $3 \times 10^{-4}$  mol/L or more and 0.01 mol/L or less.

The halogen composition in a halide solution added during nucleation is preferably  $\text{Br}^-$ ,  $\text{Cl}^-$ , and  $\text{I}^-$ , and  
20 they can be present individually or in combination. Nucleation such that the chlorine content is 10 mol% or more of the amount of the silver used for the nucleation as disclosed in JP-A-10-293372 may be employed. At this time, the concentration of  $\text{Cl}^-$  is  
25 preferably 10 mol% or more and 100 mol% or less, and more preferably 20 mol% or more and 80 mol% or less, based on the concentration of the total halides.

The protective colloid may be dissolved in a halide solution added during nucleation. Alternatively, the gelatin solution may also be added separately but simultaneously with a halide solution during nucleation.

5           The temperature in the nucleation is preferably from 5 to 60°C, but when fine tabular grains having an average grain diameter of 0.5  $\mu\text{m}$  or less are produced, the temperature is more preferably from 5 to 48°C.

10           The pH of the dispersion medium when amino group-modified gelatin is used is preferably 4 or more and 8 or less but when other gelatins are used it is preferably 2 or more and 8 or less.

## 2. Ripening step

15           In the nucleation described in 1 above, fine grains other than tabular grains are formed (in particular, octahedral and single twin grains). Accordingly, the grains other than tabular grains are necessary to be vanished before entering a growing step described infra to obtain nuclei having the forms of  
20           becoming tabular grains and good monodispersibility. For this purpose, it is well known that Ostwald ripening is conducted subsequent to the nucleation.

25           The pBr is adjusted just after nucleation, then the temperature is raised and ripening is carried out until the hexagonal tabular grain ratio reaches the maximum. At this time, protective colloid may be added additionally. The concentration of protective colloid

to the dispersion medium solution at this time is preferably 10% by weight or less. The above-described alkali-processed gelatin, amino group-modified gelatin of the present invention, oxidized gelatin, low  
5 molecular weight gelatin, natural high polymers and synthetic high polymers can be used as additional protective colloids. Further, if necessary, lime-processed ossein gelatin containing 20% or more, preferably 30% or more of components having a molecular  
10 weight of 280,000 in a molecular weight distribution determined by the Puggy's method disclosed in JP-A-11-237704 may be employed. Furthermore, for example, starches disclosed in EP No. 758758 and U.S.P. No. 5,733,718 may also be used.

15 The temperature during ripening is from 40 to 80°C, preferably from 50 to 80°C, and the pBr is from 1.2 to 3.0. The pH is preferably 4 or more and 8 or less when amino group-modified gelatin is present, and preferably 2 or more and 8 or less when other gelatins are used.

20 A silver halide solvent may be used for rapidly vanishing grains other than tabular grains. The concentration of the silver halide solvent at this time is preferably from 0.3 mol/L or less, more preferably 0.2 mol/L or less.

25 Thus, almost pure tabular grains are obtained by the ripening.

After the ripening is completed, if the silver

halide solvent is unnecessary in the next growing stage, the silver halide solvent is removed as follows.

(i) In the case of alkaline silver halide solvents such as  $\text{NH}_3$ , an acid having great solubility product with  $\text{Ag}^+$  such as  $\text{HNO}_3$  is added to be nullified.

(ii) In the case of thioether based silver halide solvent, an oxidizing agent such as  $\text{H}_2\text{O}_2$  is added to be nullified as disclosed in JP-A-60-136736.

In the production method of an emulsion of the present invention, the completion of the ripening step is defined as a time of disappearance of tabular grains (regular or single twin grains) having hexagonal or triangular main planes but not having two or more twin planes. The disappearance of tabular grains having hexagonal or triangular main planes but not having two or more twin planes can be confirmed through the observation of the TEM image of a replica of grains.

In the ripening step, an over-ripening step disclosed in JP-A-11-174606 may be provided, if necessary. The over-ripening step refers to a step where ripening (ripening step) is performed until the proportion of hexagonal tabular grains becomes maximum, and then the tabular grains subjected to Ostwald ripening, thereby eliminating tabular grains with a slow anisotropic growing rate. When letting the number of grains obtained in the ripening step be 100, it is preferable to reduce the number of tabular grains to 90

or less, and more preferable to reduce it to 60 or more and 80 or less.

In the production method of the emulsion of the present invention, conditions of pBr, temperature and the like during the over-ripening step may be set as in the ripening step. Further, in the over-ripening step, a silver halide solvent may be added as in the ripening step, and the kind, concentration and the like thereof may be set to those the same as in the ripening step.

### 3. Growing step

The pBr during the crystal growing stage subsequent to the ripening step is preferably maintained at 1.4 to 3.5. When the concentration of protective colloid in a dispersion medium solution before entering the growing step is low (1% by weight or less), protective colloid is additionally added in some cases. Further, protective colloid may be additionally added during the growing step. The timing of the addition may be any time during the growing step. The concentration of protective colloid in a dispersion medium solution at that time is preferably from 1 to 10% by weight. The above-described alkali-processed gelatin, amino group-modified gelatin of the present invention, oxidized gelatin, natural high polymers and synthetic high polymers can be used as additional protective colloids. Further, if necessary, lime-processed ossein gelatin containing 20% or more,

preferably 30% or more of components having a molecular weight of 280,000 in a molecular weight distribution determined by the Puggy's method disclosed in JP-A-11-237704 may be employed. Furthermore, for example, starches disclosed in EP No. 758758 and U.S.P. No. 5,733,718 may also be used. The pH during growing is preferably from 4 to 8 when amino group-modified gelatin is present, and preferably from 2 to 8 when other gelatins are used. The feeding rate of  $\text{Ag}^+$  and a halogen ion in the crystal growing stage is preferably adjusted to such a degree that the crystal growing speed becomes from 20 to 100%, more preferably from 30 to 100%, of the critical growing speed of the crystal. In this case, the feeding rates of a silver ion and a halogen ion are increased with the crystal growth of the grains and, as disclosed in JP-B's-48-36890 and 52-16364, the feeding rates of an aqueous solution of silver salt and an aqueous solution of halide may be increased, alternatively, the concentrations of an aqueous solution of silver salt and an aqueous solution of halide may be increased.

When performing by the double-jet method in which an aqueous silver salt solution and an aqueous halide salt solution are added simultaneously, it is preferable to stir in the reaction vessel well or to dilute the concentration of the solution to be added for preventing the introduction of growth dislocation

due to ununiformity of iodine.

A method is more preferable in which an AgI fine grain emulsion prepared outside the reaction vessel is added to the same timing when an aqueous silver salt solution and an aqueous halide salt solution are added. In this case, the temperature of growth is preferably 50°C or more and 90°C or less, and more preferably 60°C or more and 85°C or less. The AgI fine grain emulsion may be that prepared in advance. Alternatively, an AgI fine grain emulsion may be added while being prepared continuously. In this case, with respect to the preparation method, JP-A-10-43570 is available as a reference. The average grain size of the AgI emulsion to be added is 0.01  $\mu\text{m}$  or more and 0.1  $\mu\text{m}$  or less, and preferably 0.02  $\mu\text{m}$  or more and 0.08  $\mu\text{m}$  or less. The iodine composition of the base grains can be varied by adjusting the amount of the AgI emulsion to be added.

It is also possible to add silver iodobromide fine grains instead of adding an aqueous silver salt solution and an aqueous halide salt solution. In this case, base grains having a desired iodine composition are obtained by rendering the iodine amount of the fine grains equal to the iodine amount of the desired base grains. Although the silver iodobromide fine grains may be those prepared in advance, it is more preferable that the fine grains may be added while being prepared continuously. The size of the silver iodobromide fine



grains to be added is 0.005  $\mu\text{m}$  or more and 0.05  $\mu\text{m}$  or less, and preferably 0.01  $\mu\text{m}$  or more and 0.03  $\mu\text{m}$  or less. The temperature during the growth is 60°C or more and 90°C or less, and preferably from 70°C to 85°C.

5           It is also possible to combine the aforementioned ion adding method, the AgI fine grain adding method, and the AgBrI fine grain adding method.

10           In the present invention, tabular grains preferably have dislocation lines. However, for the purpose of reducing pressure desensitization, it is preferable that there are no dislocation lines in a base portion. Dislocation lines in tabular grains can be observed by a direct method using a transmission electron microscope at a low temperature described in, 15 e.g., J. F. Hamilton, Phot. Sci. Eng., 11, 57, (1967) or T. Shiozawa, J. Soc. Phot. Sci. Japan, 35, 213, (1972). That is, silver halide grains, extracted carefully from an emulsion so as not to apply a pressure at which dislocations are produced in the 20 grains, are placed on a mesh for electron microscopic observation. Observation is performed by a transmission method while the sample is cooled to prevent damage (e.g., print out) due to electron rays. In this case, the greater the thickness of a grain, the 25 more difficult it becomes to transmit electron rays through it. Therefore, grains can be observed more clearly by using an electron microscope of high voltage

type (200 kV or more for a grain having a thickness of 0.25  $\mu\text{m}$ ). From photographs of grains obtained by the above method, it is possible to obtain the positions and the number of dislocation lines in each grain viewed in a direction perpendicular to the main planes of the grain.

Next, step (b) will be described.

First, step (b1) will be described. Step (b1) comprises a first shell step and a second shell step. A first shell is formed on the base described above. The ratio of the first shell is 1% or more and 30% or less of the total silver amount, and the average silver iodide content of the first shell is 20 mol% or more and 100 mol% or less. More preferably, the ratio of the first shell is 1% or more and 20% or less of the total silver amount, and the average silver iodide content of the first shell is preferably 25 mol% or more and 100 mol% or less. The growth of the first shell on a base is basically performed by the addition of an aqueous silver nitrate solution and an aqueous halogen solution containing both iodide and bromide by the double-jet method, or by the addition of an aqueous silver nitrate solution and an aqueous halogen solution containing iodide by the double-jet method. Alternatively, an aqueous halogen solution containing iodide is added by the single-jet method.

Any of these methods may be applied, and any

combination thereof may also be applied. As is clear from the average silver iodide content of the first shell, silver iodide can also precipitate in addition to a silver iodobromide mixed crystal during the formation of the first shell. In either case, the silver iodide vanishes and entirely changes into a silver iodobromide mixed crystal during the formation of the second shell.

A preferable method for the formation of the first shell is a method comprising adding a silver iodobromide or silver iodide fine grain emulsion, ripening and dissolving. Another preferable method is a method comprising adding a silver iodide fine grain emulsion, followed by the addition of an aqueous silver nitrate solution or addition of aqueous silver nitrate solution and an aqueous halogen solution. In this case, the dissolution of the silver iodide fine grain emulsion is accelerated by the addition of the aqueous silver nitrate solution. The silver amount of the added silver iodide fine grain emulsion is used to obtain the first shell, and the silver iodide content thereof is assumed to be 100 mol%. The amount of silver of the added aqueous silver nitrate solution is used to calculate the second shell. It is preferable that the silver iodide fine grain emulsion is added abruptly.

"To add a silver iodide fine grain emulsion

abruptly adding" is to add the silver iodide fine grain emulsion preferably within 10 minutes, and more preferably, within 7 minutes. This condition may vary in accordance with, e.g., the temperature, pBr, and pH of the system to which the emulsion is added, the type and concentration of a protective colloid agent such as gelatin, and the presence/absence, type, and concentration of a silver halide solvent. However, a shorter addition time is more preferable as described above. During the addition, it is preferable that an aqueous solution of silver salt such as silver nitrate is not substantially added. The temperature of the system during the addition is preferably 40°C or more and 90°C or less, and most preferably, 50°C or more and 80°C or less.

A silver iodide fine grain emulsion essentially need only be silver iodide and can contain silver bromide and/or silver chloride as long as a mixed crystal can be formed. The emulsion is preferably 100% silver iodide. The crystal structure of silver iodide can be a  $\beta$  body, a  $\gamma$  body, or, as described in US4,672,026, the disclosure of which is herein incorporated by reference, an  $\alpha$  body or an  $\alpha$  body similar structure. In the present invention, the crystal structure is not particularly restricted but is preferably a mixture of  $\beta$  and  $\gamma$  bodies, and more preferably, a  $\beta$  body. The silver iodide fine grain

emulsion can be either an emulsion formed immediately before addition described in US5,004,679 the disclosure of which is herein incorporated by reference, or an emulsion subjected to a regular washing step. In the present invention, an emulsion subjected to a regular washing step is used. The silver iodide fine grain emulsion can be readily formed by a method described in, e.g., aforementioned US4,672,026. A double-jet addition method using an aqueous silver salt solution and an aqueous iodide salt solution in which grain formation is performed with a fixed pI value is preferred. The pI is the logarithm of the reciprocal of the  $I^-$  ion concentration of the system. The temperature, pI, and pH of the system, the type and concentration of a protective colloid agent such as gelatin, and the presence/absence, type, and concentration of a silver halide solvent are not particularly limited. However, a grain size of preferably  $0.1 \mu m$  or less, and more preferably,  $0.07 \mu m$  or less is convenient for the present invention. Although the grain shapes cannot be perfectly specified because the grains are fine grains, the variation coefficient of a grain size distribution is preferably 25% or less. The effect of the present invention is particularly remarkable when the variation coefficient is 20% or less. The sizes and the size distribution of the silver iodide fine grain emulsion are obtained by

laying silver iodide fine grains on a mesh for electron  
microscopic observation and directly observing the  
grains by a transmission method instead of a carbon  
replica method. This is because measurement errors are  
5 increased by observation done by the carbon replica  
method since the grain sizes are small. The grain size  
is defined as the diameter of a circle having an area  
equal to the projected surface area of the observed  
grain. The grain size distribution also is obtained by  
10 using this equivalent-circle diameter of the projected  
surface area. In the present invention, the most  
effective silver iodide fine grains have a grain size  
of 0.06 to 0.02  $\mu\text{m}$  and a grain size distribution  
variation coefficient of 18% or less.

15 After the grain formation described above,  
a silver iodide fine grain emulsion is preferably  
subjected to regular washing described in, e.g.,  
US2,614,929, the disclosure of which is herein  
incorporated by reference, and adjustments of the pH,  
20 the pI, the concentration of a protective colloid agent  
such as gelatin, and the concentration of the contained  
silver iodide are performed. The pH is preferably 5  
to 7. The pI value is preferably the one at which the  
solubility of silver iodide is a minimum or the one  
25 higher than that value. As the protective colloid  
agent, a common gelatin having an average molecular  
weight of approximately 100,000 is preferably used.

A low-molecular-weight gelatin having an average molecular weight of 20,000 or less also is preferably used. It is sometimes convenient to use a mixture of gelatins having different molecular weights.

5 The gelatin amount is preferably 10 to 100g, and more preferably, 20 to 80g per kg of an emulsion. The silver amount is preferably 10 to 100g, and more preferably, 20 to 80g, in terms of silver atoms, per kg of an emulsion. As the gelatin amount and/or the  
10 silver amount, it is preferable to choose values suited to abrupt addition of the silver iodide fine grain emulsion.

The silver iodide fine grain emulsion is usually dissolved before being added. During the addition it  
15 is necessary to sufficiently raise the efficiency of stirring of the system. The rotating speed of stirring is preferably set to be higher than usual. The addition of an antifoaming agent is effective to prevent the formation of foam during the stirring.  
20 More specifically, an antifoaming agent described in, e.g., examples of US5,275,929 is used.

As a more preferable method for forming the first shell, it is possible to form a silver halide phase containing silver iodide while causing iodide ions to  
25 generate abruptly by using an iodide ion releasing agent described in U.S.P. No. 5,496,694, instead of the conventional iodide ion supply method (the method of

adding free iodide ions).

The iodide ion-releasing agent releases iodide ions through its reaction with an iodide ion release control agent (a base and/or a nucleophilic reagent).

5 Preferable examples of this nucleophilic reagent used include the following chemical species, e.g., hydroxide ion, sulfite ion, hydroxylamine, thiosulfate ion, metabisulfite ion, hydroxamic acids, oximes, dihydroxybenzenes, mercaptanes, sulfinates, carboxylate,  
10 ammonia, amines, alcohols, ureas, thioureas, phenols, hydrazines, hydrazides, semicarbazides, phosphines and sulfides.

The release rate and timing of iodide ions can be controlled through the control of the concentration and  
15 addition method of a base or a nucleophilic reagent or the control of the temperature of the reaction solution. A preferable base is alkali hydroxide.

To generate iodide ions abruptly, the concentrations of the iodide ion-releasing agent and  
20 iodide ion release control agent are preferably  $1 \times 10^{-7}$  to 20 M, more preferably,  $1 \times 10^{-5}$  to 10 M, further preferably,  $1 \times 10^{-4}$  to 5 M, and particularly preferably,  $1 \times 10^{-3}$  to 2 M.

If the concentration exceeds 20 M, the addition  
25 amounts of the iodide ion-releasing agent and iodide ion release control agent having large molecular weights adversely become too great compared to the



capacity of the grain formation vessel.

If the concentration is less than  $1 \times 10^{-7}$  M, the iodide ion-releasing reaction rate adversely becomes too low, and this makes it difficult to abruptly  
5 generate the iodide ion-releasing agent.

The temperature is preferably 30 to 80, more preferably, 35 to 75°C, and particularly preferably, 35 to 60°C.

At high temperatures exceeding 80°C, the iodide  
10 ion-releasing reaction rate generally becomes extremely high. At low temperatures below 30°C, the iodide ion-releasing reaction temperature generally becomes extremely low. Both cases are undesirable because the use conditions are restricted.

15 When a base is used to release iodide ions, a change in the solution pH can also be used. If this is the case, the pH range for controlling the rate and timing of releasing iodide ions is preferably 2 to 12, more preferably 3 to 11, and particularly preferably 5  
20 to 10. Most preferably, the pH after adjustment is 7.5 to 10.0. Under a neutral condition of pH 7, hydroxide ions having a concentration determined by the ion product of water function as control agents.

A nucleophilic reagent and a base can be used  
25 jointly. When this is the case, the pH can be controlled within the above range to thereby control the rate and timing of releasing iodide ions.

When iodine atoms are to be released in the form of iodide ions from the iodide ion-releasing agent, these iodine atoms may be entirely released or may partially remain without decomposition.

5           The second shell is formed on the above-described base and a tabular grain having the first shell. The ratio of the second shell is 10 mol% or more and 40 mol% or less of the total silver amount, and the average silver iodide content of the second shell is 0  
10 mol% or more and 5 mol% or less. More preferably, the ratio of the second shell is 15 mol% or more and 30 mol% or less of the total silver amount, and the average silver iodide content of the fourth shell is 0  
15 mol% or more and 3 mol% or less. The growth of the second shell on a base and a tabular grain having the first shell can be performed either in a direction to increase the aspect ratio of the tabular grain or in a direction to decrease it. The growth of the second  
20 shell is basically performed by addition of an aqueous silver nitrate solution and an aqueous halogen solution containing bromide using the double-jet method. Alternatively, it is also possible to add an aqueous silver halogen solution containing bromide and then add an aqueous silver nitrate solution by the single-jet  
25 method. The temperature and pH of the system, the type and concentration of a protective colloid agent such as gelatin, and the presence/absence, type, and

concentration of a silver halide solvent may vary over a broad range. With respect to pBr, the pBr at the end of the formation of the second shell layer is preferably higher than that in the initial stages of the formation of that layer. Preferably, the pBr in the initial stages of the formation of the layer is 2.9 or less, and the pBr at the end of the formation of the layer is 1.7 or more. More preferably, the pBr in the initial stages of the formation of the layer is 2.5 or less, and the pBr at the end of the formation of the layer is 1.9 or more. Most preferably, the pBr in the initial stages of the formation of the layer is 1 or more and 2.3 or less and the pBr at the end of the formation of the layer is 2.1 or more and 4.5 or less.

It is preferable that there are dislocation lines in the portion of step (b1). The dislocation lines are preferably present in the vicinities of the side faces of tabular grains. The vicinities of the side faces refer to the six side faces of a tabular grain and the area inside the faces, that is, the portion grown in step (b1). The average number of the dislocation lines present in the side faces is preferably 10 or more, and more preferably 20 or more per grain. If dislocation lines are densely present or they are observed to cross each other, it is sometimes impossible to correctly count dislocation lines per grain. Even in such situations, however, dislocation lines can be roughly

counted to such an extent as in units of 10 lines, like 10, 20, or 30 dislocation lines, thereby making it possible to distinguish these grains from those in which obviously only a few dislocation lines are present. The average number of dislocation lines per grain is obtained as a number average by counting dislocation lines for 100 or more grains.

The dislocation line amount distribution is preferably uniform between tabular grains of the present invention. In an emulsion of the present invention, silver halide grains containing 10 or more dislocation lines per grain account for preferably 100 to 50%, more preferably, 100 to 70%, and most preferably, 100 to 90%.

A percentage lower than 50% is undesirable in respect of homogeneity between grains.

To obtain the ratio of grains containing dislocation lines and the number of dislocation lines in the present invention, it is preferable to directly observe dislocation lines for 100 grains or more, more preferably 200 grains or more, and particularly preferably 300 grains or more.

Next, step (b2) will be described.

Step (b2) includes the following embodiments: as a first embodiment, a method comprising dissolving only the vicinities of apexes with iodide ions; as a second embodiment, a method comprising adding a silver salt

solution and an iodide salt solution simultaneously; as  
a third embodiment, a method comprising substantially  
dissolving only the vicinities of apexes with a silver  
halide solvent; and as a forth embodiment, a method via  
5 halogen conversion.

The first embodiment, the method of dissolving  
with iodide ions will be described below.

When iodide ions are added to base grains, the  
vicinity of each apex portion of the base grains is  
10 dissolved and the grains are somewhat rounded. When,  
successively, a silver nitrate solution and a bromide  
solution, or a silver nitrate solution and a mixed  
solution comprising a bromide solution and an iodide  
solution are added simultaneously, the grains further  
15 grow and dislocation is introduced in the vicinities of  
the apexes. With respect to this method, JP-A's-4-  
149541 and 9-189974 are available as references.

For attaining an effective dissolution according  
to the present embodiment, it is preferable that when  
20 the value obtained by multiplying, by 100, the quotient  
resulting from dividing the number of the whole iodide  
ions by the mol number of the total silver in the base  
grains is let be  $I_2$  (mol%), the total amount of the  
iodide ions to be added in this embodiment satisfies  
25 the condition in which  $(I_2 - I_1)$  is 0 or more and 8 or  
less, and more preferably 0 or more and 4 or less, with  
respect to the silver iodide content of the base grains

$I_1$  (mol%).

The lower the concentration of the iodide ions to be added in this embodiment, the more preferable. Specifically, the concentration is preferably 0.2 mol/L or less, and more preferably 0.1 mol/L or less.

pAg during the addition of iodide ions is preferably 8.0 or more, and more preferably 8.5 or more.

Following the dissolution of the apex portions of the base grains by the addition of iodide ion to the base grains, the grains are further grown so that dislocation is introduced in the vicinities of the apexes by the addition of a silver nitrate solution or the simultaneous addition of a silver nitrate solution and a bromide solution or a silver nitrate solution and a mixed solution comprising a bromide solution and an iodide solution.

The second embodiment, the method comprising adding a silver salt solution and an iodide salt solution simultaneously will be described below. By rapidly adding a silver salt solution and an iodide salt solution to base grains, it is possible to epitaxially generate silver iodide or a silver halide having a high silver iodide content at apex portions of the grains. At this time, the addition rates of the silver salt solution and the iodide salt solution are preferably 0.2 min. or more and 0.5 min. or less, more preferably 0.5 min. or more and 2 min. or less. This

method is disclosed in JP-A's-4-149541 and therefore the publication is available as a reference.

Following the dissolution of the apex portions of the base grains by the addition of iodide ion to the base grains, the grains are further grown so that dislocation is introduced in the vicinities of the apexes by the addition of a silver nitrate solution or the simultaneous addition of a silver nitrate solution and a bromide solution or a silver nitrate solution and a mixed solution comprising a bromide solution and an iodide solution.

The third embodiment, the method using a silver halide solvent will be described below.

When a silver halide solvent is added to a dispersion medium containing base grains and then a silver salt solution and an iodide salt solution are added simultaneously, silver iodide or a silver halide having a high silver iodide content preferentially grows at apex portions of the base grains dissolved with the silver halide solvent. In this operation, it is not necessary to add the silver salt solution or the iodide salt solution rapidly. This method is disclosed in JP-A's-4-149541 and therefore the publication is available as a reference.

Following the dissolution of the apex portions of the base grains by the addition of iodide ion to the base grains, the grains are further grown so that

dislocation is introduced in the vicinities of the apexes by the addition of a silver nitrate solution or the simultaneous addition of a silver nitrate solution and a bromide solution or a silver nitrate solution and a mixed solution comprising a bromide solution and an iodide solution.

Next, the forth embodiment, the method via halogen conversion will be described.

This is a method in which an epitaxially growing site director (hereinafter, referred to as a site director), such as a sensitizing dye disclosed in JP-A-58-108526 and a water-soluble iodide, is added to base grains so that epitaxial of silver chloride is formed at the apex portions of the base grains and then iodide ions are added so that the silver chloride is halogen converted into silver iodide or silver halide having a high silver iodide content. As the site director, sensitizing dyes, a water-soluble thiocyanate ion and water-soluble iodide ion can be used, and the iodide ion is preferable. The iodide ion is used in an amount of 0.0005 to 1 mol%, and preferably 0.001 to 0.5 mol% of the base grains. When the optimum amount of iodide ion is added and then a silver salt solution and a chloride salt solution are added simultaneously, epitaxial of silver chloride can be formed at apex portions of the base grains.

The following is a description on halogen



conversion of silver chloride caused by iodide ions. A silver halide having a great solubility is converted into a silver halide having a less solubility by addition of halide ions capable of forming the silver halide having a less solubility. This process is called halogen conversion and is disclosed in U.S.P. No. 4,142,900. By selectively subjecting the silver chloride epitaxially grown at apex portions of the base to halogen conversion with iodide ions, a silver iodide phase is formed at apex portions of the base grains. The detail will be disclosed in JP-A-4-149541.

Following the halogen conversion of the silver chloride epitaxially grown at apex portions of the base grains into a silver iodide phase caused by the addition of iodide ions, the grains are further grown so that dislocation is introduced in the vicinities of the apexes by the addition of a silver nitrate solution or the simultaneous addition of a silver nitrate solution and a bromide solution or a silver nitrate solution and a mixed solution comprising a bromide solution and an iodide solution.

It is preferable that there are dislocation lines in the portion of step (b2). The dislocation lines are preferably present in the vicinities of the apex portions of tabular grains. The vicinity of an apex portion of a grain refers to the three-dimensional portion defined in the following manner.

Perpendiculars are dropped each from a point located on a straight line connecting the center of the grain and  $x\%$  away from the center of the straight line to each of the sides of the grain defining the apex. The above

5 perpendiculars and the above sides surround a three-dimensional portion. The value of  $x$  is preferably 50 or more and less than 100, and more preferably 75 or more and less than 100. The average number of the

10 dislocation lines present in the edge portions is preferably 10 or more, and more preferably 20 or more per grain. If dislocation lines are densely present or they are observed to cross each other, it is sometimes impossible to correctly count dislocation lines per

15 grain. Even in such situations, however, dislocation lines can be roughly counted to such an extent as in units of 10 lines, like 10, 20, or 30 dislocation lines, thereby making it possible to distinguish these grains from those in which obviously only a few dislocation

20 lines are present. The average number of dislocation lines per grain is obtained as a number average by counting dislocation lines for 100 or more grains.

The dislocation line amount distribution is preferably uniform between tabular grains of the present invention. In an emulsion of the present

25 invention, silver halide grains containing 10 or more dislocation lines per grain account for preferably 100 to 50%, more preferably, 100 to 70%, and most

preferably, 100 to 90%.

A percentage lower than 50% is undesirable in respect of homogeneity between grains.

To obtain the ratio of grains containing  
5 dislocation lines and the number of dislocation lines in the present invention, it is preferable to directly observe dislocation lines for 100 grains or more, more preferably 200 grains or more, and particularly preferably 300 grains or more.

10 Next, step (b3) will be described.

About the epitaxial formation of silver halide to base grains, U.S.P. No. 4,435,501 discloses that silver salt epitaxial can be formed at selected sites, e.g., apex portions or side face portions of base grains, by  
15 a site director such as iodide ions, aminoazaindene or spectral sensitizing dyes adsorbed to the surface of the base grains. In JP-A-8-69069, the enhancement of sensitivity is attained by forming silver salt epitaxial at selected sites in extremely thin tabular  
20 grains and subjecting the epitaxial phase to optimum chemical sensitization.

Also in the present invention, it is very preferable to enhance the sensitivity of the base grains of the present invention using these methods.  
25 As the site director, aminoazaindene or spectral sensitizing dyes may be used and iodide ions or thiocyanate ions may also be used. These may be

properly used depending on the purposes, or may be used in combination.

By varying the addition amounts of the sensitizing dyes, sensitizing ions and thiocyanate ions, the site  
5 for forming silver salt epitaxial can be limited to the main plane portions, the side face portions or the apex portions of base grains. Combinations of them are also possible. It is preferable that the amounts of aminoazaindene, iodide ions, thiocyanate ions and  
10 spectral sensitizing dyes are suitably selected depending on the silver amount and the surface area of the silver halide base grains to be used, and the limited sites of epitaxial. The temperature at which silver salt epitaxial is formed is preferably 40 to  
15 70°C, and more preferably 45 to 60°C. At this time, pAg is preferably 9.0 or less, and more preferably 8.0 or less. By suitably selecting the kind and addition amount of site directors and epitaxial deposition conditions (e.g., temperature and pAg) in such a manner,  
20 epitaxial of silver salt can be formed selectively on the main plane portions, side face portions or apex portions. The thus obtained emulsion may be enhanced its sensitivity by being subjected to chemical sensitization selectively in its epitaxial phase as in  
25 JP-A-8-69069, and also may be further grown by means of simultaneous addition of a silver salt solution and a halide salt solution following the silver salt

epitaxial formation. As the aqueous halide salt solution to be added in this treatment, a bromide salt solution, or a mixed solution comprising a bromide salt solution and an iodide salt solution is preferable. In  
5 the treatment, the temperature is preferably 40 to 80°C, and more preferably 45 to 70°C. At this time, pAg is preferably 5.5 or more and 9.5 or less, and more preferably 6.0 or more and 9.0 or less. Furthermore, it is also possible to perform halogen conversion of  
10 the epitaxial by adding a halogen solution different from the epitaxial composition. The epitaxial formation and the subsequent growth, or the halogen conversion may be performed successively after the silver halide base grain formation, and also may be  
15 performed after washing with water/re-dispersion following the base grain formation. They also may be performed before chemical sensitization. The epitaxial formation and the subsequent growth, or the halogen conversion may be carried out separately before and  
20 after the washing with water/re-dispersion.

The epitaxial formed in step (b3) is characterized by projecting outside the base grains formed in step (a). The composition of epitaxial is preferably AgBr, AgCl, AgBrCl, AgBrClI, AgBrI, AgI, AgSCN, or the like.  
25 It is more preferable to introduce a "dopant (metal complex)" such as those disclosed in JP-A-8-69069, to an epitaxial layer. The position of epitaxial growth

may be at least a part of the apex portions, the side face portions and the main plane portions of the base grains and also may be spread over two or more portions. The apex portion refers to each apex of a triangular or hexagonal, tabular grain (six apexes for a hexagon and three apexes for a triangle). It is preferable that at least one of the apexes has the epitaxial. The side face portion refers to, in the case of a hexagonal tabular grain, the six sides and the planes connecting the two main plane portions, namely side face portions. The epitaxial may be present in any portion of six sides and side face portions. It is only required that at least one epitaxial is present. The same are true for the case of triangle tabular grains. The main plane portion refers to two main planes in a tabular grain. The epitaxial may be present at any position in the main planes. It is only required that at least one epitaxial is present. With respect to the shape of the epitaxial, a {100} face, a {111} face, or a {110} face may appear alone. Alternatively, two or more of the faces may appear. Further, the epitaxial may have an amorphous structure where faces of a higher order appear.

No dislocation lines are required to be present in the portion of step (b3), but it is more preferable that there is a dislocation line. It is preferable for dislocation lines to be present in the connecting

portion between a base grain and an epitaxial growth portion or in an epitaxial portion. The average number of the dislocation lines present in the connecting portions or epitaxial portions is preferably 10 or more, and more preferably 20 or more per grain. If dislocation lines are densely present or they are observed to cross each other, it is sometimes impossible to correctly count dislocation lines per grain. Even in such situations, however, dislocation lines can be roughly counted to such an extent as in units of 10 lines, like 10, 20, or 30 dislocation lines, thereby making it possible to distinguish these grains from those in which obviously only a few dislocation lines are present. The average number of dislocation lines per grain is obtained as a number average by counting dislocation lines for 100 or more grains.

It is preferable that the system is doped with a hexacyanometal complex during the formation of an epitaxial portion. Of hexacyanometal complexes, those containing iron, ruthenium, osmium, cobalt, rhodium, iridium or chromium are preferable. The addition amount of such a metal complex is preferably with in the range of from  $10^{-9}$  to  $10^{-2}$  mol per mol of silver halide, and more preferably within the range of from  $10^{-8}$  to  $10^{-4}$  mol per mol of silver halide. The metal complex may be added after being dissolved in water or an organic solvent. The organic solvent preferably has

a miscibility with water. Examples of the organic solvent includes alcohol, ether, glycol, ketone, ester and amide.

5 The dislocation line amount distribution is preferably uniform between tabular grains of the present invention. In an emulsion of the present invention, silver halide grains containing 5 or more dislocation lines per grain account for preferably 100 to 50%, more preferably, 100 to 70%, and most  
10 preferably, 100 to 90%.

A percentage lower than 50% is undesirable in respect of homogeneity between grains.

To obtain the ratio of grains containing dislocation lines and the number of dislocation lines  
15 in the present invention, it is preferable to directly observe dislocation lines for 100 grains or more, more preferably 200 grains or more, and particularly preferably 300 grains or more.

As a protective colloid and as a binder of other  
20 hydrophilic colloid layers that are used when the emulsion according to the present invention is prepared, gelatin is used advantageously, but another hydrophilic colloid can also be used.

Use can be made of, for example, a gelatin  
25 derivative, a graft polymer of gelatin with another polymer, a protein, such as albumin and casein; a cellulose derivative, such as hydroxyethylcellulose,



carboxymethylcellulose, and cellulose sulfate ester;  
sodium alginate, a saccharide derivative, such as a  
starch derivative; and many synthetic hydrophilic  
polymers, including homopolymers and copolymers, such  
5 as a polyvinyl alcohol, a polyvinyl alcohol partial  
acetal, a poly-N-vinylpyrrolidone, a polyacrylic acid,  
a polymethacrylic acid, a polyacrylamide, a  
polyvinylimidazole and a polyvinylpyrazole.

Preferably, the silver halide emulsion according  
10 to the present invention is washed with water for  
desalting and is dispersed in a freshly prepared  
protective colloid. Gelatin is used as protective  
colloid but natural high polymers besides gelatin and  
synthetic high polymers can also be used. Alkali-  
15 processed gelatin, oxidized gelatin, i.e., gelatin in  
which a methionine group in the gelatin molecule is  
oxidized with hydrogen peroxide, etc. (a methionine  
content of 40  $\mu\text{mol/g}$  or less) and amino group-modified  
gelatin of the present invention (e.g., phthalated  
20 gelatin, trimellitated gelatin, succinated gelatin,  
maleated gelatin, and esterified gelatin). Further, if  
necessary, lime-processed ossein gelatin containing 20%  
or more, preferably 30% or more of components having a  
molecular weight of 280,000 in a molecular weight  
25 distribution determined by the Puggy's method  
disclosed in JP-A-11-237704 may be employed.  
Furthermore, for example, starches disclosed in EP No.

758758 and U.S.P. No. 5,733,718 may also be used.

Further, natural high polymers will be described in JP-B-7-111550 and Research Disclosure, Vol. 176, No. 17643, item IX (December, 1978). The temperature at which the

5 washing with water is carried out can be selected in accordance with the purpose, and preferably the temperature is selected in the range of 5°C to 50°C.

The pH at which the washing with water is carried out can be selected in accordance with the purpose, and  
10 preferably the pH is selected in the range of 2 to 10, and more preferably in the range of 3 to 8. The pAg at which the washing with water is carried out can be selected in accordance with the purpose, and preferably  
the pAg is selected in the range of 5 to 10. As a

15 method of washing with water, it is possible to select from the noodle washing method, the dialysis method using a diaphragm, the centrifugation method, the coagulation settling method, the ion exchange method and the ultrafiltration. In the case of the  
20 coagulation settling method, selection can be made from, for example, the method wherein sulfuric acid salt is used, the method wherein an organic solvent is used, the method wherein a water-soluble polymer is used, and the method wherein a gelatin derivative is used.

25 During the grain formation of the present invention, it is possible to cause a polyalkyleneoxide block copolymer disclosed in, for example, JP-A's-5-

173268, 5-173269, 5-173270, 5-173271, 6-202258 and 7-175147, or a polyalkyleneoxide copolymer disclosed in Japanese Patent No. 3089578 to exist. Such a compound exists may exist at any timing during the preparation  
5 of the grains. However, its use in early stages of grain formation exhibits a great effect.

A third emulsion relating to the present invention, comprising tabular silver halide grains of silver iodobromide or silver chloriodobromide whose  
10 silver chloride content is less than 10 mol%, and having (100) faces as parallel main planes will be described below.

With respect to the (100) tabular grains of the present invention, 50 to 100%, preferably 70 to 100%,  
15 and more preferably 90 to 100%, of the total projected area is occupied by tabular grains having (100) faces as main planes and having an aspect ratio of 2 or more. The grain thickness is preferably in the range of 0.01 to 0.10  $\mu\text{m}$ , more preferably 0.02 to 0.08  $\mu\text{m}$ , and most  
20 preferably 0.03 to 0.07  $\mu\text{m}$ . The aspect ratio is preferably in the range of 2 to 100, more preferably 3 to 50, and most preferably 5 to 30. The variation coefficient of grain thickness (percentage of "standard deviation of distribution/average grain thickness",  
25 hereinafter referred to as "COV") is preferably 30% or less, more preferably 25% or less, and most preferably 20% or less. The smaller this COV, the higher the

monodispersity of grain thickness.

In the measuring the equivalent circle diameter and thickness of tabular grains, a transmission electron micrograph (TEM) thereof is taken according to the replica method, and the equivalent circle diameter and thickness of each individual grain are measured. In this method, the thickness of tabular grains is calculated from the length of shadow of the replica. In the present invention, the COV is determined as a result of measuring at least 600 grains.

The silver halide composition of the (100) tabular grains of the present invention is silver iodobromide or silver chloriodobromide having a silver chloride content of less than 10 mol%. Furthermore, other silver salts, such as silver rhodanate, silver sulfide, silver selenide, silver telluride, silver carbonate, silver phosphate and an organic acid salt of silver, may be contained in the form of other separate grains or as parts of silver halide grains.

The X-ray diffraction method is known as means for investigating the halogen composition of AgX crystals. The X-ray diffraction method is described in detail in, for example, Kiso Bunseki Kagaku Koza 24 (Fundamental Analytical Chemistry Course 24) "X-sen Kaisetu (X-ray Diffraction)". In the standard method, K $\beta$  radiation of Cu is used as a radiation source, and the diffraction angle of AgX (420) face is determined by the powder

method.

When the diffraction angle  $2\theta$  is determined, the lattice constant (a) can be determined by Bragg's equation as follows:

5             $2 d \sin\theta = \lambda$   
             $d = a / (h^2 + k^2 + l^2)^{1/2},$

            wherein  $2\theta$  represents the diffraction angle of  
            (hkl) face;  $\lambda$  represents the wavelength of X rays; and  
            d represents the spacing of (hkl) faces. Because, with  
10            respect to silver halide solid solutions, the  
            relationship between the lattice constant (a) and the  
            halogen composition is known (described in, for  
            example, T.H. James "The Theory of the Photographic  
            Process, 4th ed.", Macmillian, New York), determination  
15            of the lattice constant leads to determination of the  
            halogen composition.

            The halogen composition structure of (100) tabular  
            grains according to the present invention is not  
            limited. Examples thereof include grains having a  
20            core/shell double structure wherein the halogen  
            compositions of the core and the shell are different  
            from each other and grains having a multiple structure  
            composed of a core and two or more shells. The core is  
            preferably constituted of silver bromide, to which,  
25            however, the core of the present invention is not  
            limited. With respect to the composition of the shell,  
            it is preferred that the silver iodide content be

higher therein than in the core.

It is preferred that the (100) tabular grains of the present invention have an average silver iodide content of 2.3 mol% or more and an average silver iodide content, at the surface of grains, of 8 mol% or more. With respect to the (100) tabular grains of the present invention, preferably, the upper limit of average silver iodide content is 20 mol% and the upper limit of average surface silver iodide content is also 20 mol%. The intergranular variation coefficient of silver iodide content is preferably less than 20%. The surface silver iodide content, can be measured by above-mentioned XPS.

The (100) tabular grains of the present invention can be classified by shape into the following six types of grains. (1) Grains whose main plane shape is a right-angled parallelogram. (2) Grains whose main plane shape is a right-angled parallelogram having one or more, preferably 1 to 4 corners selected from four corners of which are non-equivalently deleted, namely, grains whose  $K1 = (\text{area of maximum deletion}) / (\text{area of minimum deletion})$  is 2 to  $\infty$ . (3) Grains whose main plane shape is a right-angled parallelogram having four corners of which are equivalently deleted (grains whose  $K1$  is smaller than 2). (4) Grains whose 5 to 100%, preferably 20 to 100% of the side of faces in the deletions one (111) faces. (5) Grains having main

planes each with four sides, of which at least two sides opposite to each other are outward protruding curves. (6) Grains whose main plane shape is a right-angled parallelogram having one or more, preferably 1 to 4 corners selected from four corners of which are deleted in the shape of a right-angled parallelogram. These features of the grains can be identified by observation through an electron microscope.

With respect to the (100) tabular grains of the present invention, the ratio of (100) faces to surface crystal habits is 80% or more, preferably 90% or more. A statistical estimation of the ratio can be performed by the use of an electron micrograph of grains. When the (100) tabular face ratio of AgX grains of an emulsion is nearly 100%, the above estimate can be ascertained by the following method. The method is described in Journal of the Chemical Society of Japan, 1984 No.6, page 942, which comprises causing a given amount of (100) tabular grains to adsorb varied amounts of benzothiacyanine dye at 40°C for 17 hr, determining the sum total (S) of surface areas of all grains and the sum total (S1) of areas of (100) faces per unit emulsion from light absorption at 625 nm, and calculating the (100) face ratio by applying these sum total values to the formula:  $(S1/S) \times 100 (\%)$ .

The average equivalent sphere diameter of the (100) tabular grains of the invention is preferably

0.35 $\mu$ m or less. The estimation of the grain size can be conducted by measuring projected areas and thickness by the replica method.

5 A fourth emulsion relating to the invention, silver halide grains having (111) faces or (100) faces as parallel main planes, having an aspect ratio of 2 or more and containing silver chloride in an amount of at least 80 mol%, will be explained below.

10 Special measures must be implemented for producing (111) grains of high silver chloride content. Use may be made of the method of producing tabular grains of high silver chloride content with the use of ammonia as described in U.S.P. No. 4,399,215 to Wey. Also, use may be made of the method of producing tabular grains  
15 of high silver chloride content with the use of a thiocyanate as described in U.S.P. No. 5,061,617 to Maskasky. Further, use may be made of the following methods of incorporating additives (crystal habit-controlling agents) at the time of grain formation in  
20 order to form grains of high silver chloride content having (111) faces as external surfaces:

	Patent No.	crystal habit-controlling agent	Inventor
25	U.S.P. 4,400,463	azaindene + thioether peptizer	Maskasky
	U.S.P. 4,783,398	2,4-dithiazolidinone	Mifune et al.
	U.S.P. 4,713,323	aminopyrazolopyrimidine	Maskasky
	U.S.P. 4,983,508	bispyridinium salt	Ishiguro et al.



	U.S.P. 5,185,239	triaminopyrimidine	Maskasky
	U.S.P. 5,178,997	7-azaindole compound	Maskasky
	U.S.P. 5,178,998	xanthine	Maskasky
	JP-A-64-70741	dye	Nishikawa et al.
5	JP-A-3-212639	aminothioether	Ishiguro
	JP-A-4-283742	thiourea derivative	Ishiguro
	JP-A-4-335632	triazolium salt	Ishiguro
	JP-A-2-32	bispyridinium salt	Ishiguro et al.
	JP-A-8-227117	monopyridinium salt	Ozeki et al.

10           With respect to the formation of (111) tabular grains, although various methods of using crystal habit-controlling agents are known as listed in the above table, the compounds (compound examples 1 to 42) described in JP-A-2-32 are preferred, and the crystal  
15           habit-controlling agents 1 to 29 described in JP-A-8-227117 are especially preferred. However, the present invention is in no way limited to these.

          The (111) tabular grains are obtained by forming two parallel twinned crystal faces. The formation of  
20           such twin faces is influenced by the temperature, dispersion medium (gelatin), halide concentration, etc., so that appropriate conditions must be set on these. In the presence of a crystal habit-controlling agent at the time of nucleation, the gelatin  
25           concentration is preferably in the range of 0.1 to 10%. The chloride concentration is 0.01 mol/liter or more, preferably 0.03 mol/liter (liter hereinafter referred

to as "L") or more.

JP-A-8-184931 discloses that, for monodispersing grains, it is preferred not to use any crystal habit-controlling agent at the time of nucleation. When no  
5 crystal habit-controlling agent is used at the time of nucleation, the gelatin concentration is in the range of 0.03 to 10%, preferably 0.05 to 1.0%. The chloride concentration is in the range of 0.001 to 1 mol/L, preferably 0.003 to 0.1 mol/L. The nucleation  
10 temperature, although can arbitrarily be selected as long as it is in the range of 2 to 90°C, is preferably in the range of 5 to 80°C, more preferably 5 to 40°C.

Nuclei of tabular grains are formed at the initial stage of nucleation. However, a multiplicity of non-  
15 tabular grain nuclei are contained in the reaction vessel immediately after the nucleation. Therefore, such a technology that, after the nucleation, ripening is carried out to thereby cause only tabular grains to remain while other grains are eliminated is required.  
20 When the customary Ostwald ripening is performed, nuclei of tabular grains are also dissolved and eliminated, so that the number of nuclei of tabular grains is reduced with the result that the size of obtained tabular grains is increased. In order to  
25 prevent this, a crystal habit-controlling agent is added. In particular, the simultaneous use of gelatin phthalate enables increasing the effect of the crystal

habit-controlling agent and thus enables preventing the dissolution of tabular grains. The pAg during the ripening is especially important, and is preferably in the range of 60 to 130 mV with silver/silver chloride electrodes.

The thus formed nuclei are subjected to physical ripening and are grown in the presence of a crystal habit-controlling agent by adding a silver salt and a halide thereto. In the system, the chloride concentration is 5 mol/L or less, preferably in the range of 0.05 to 1 mol/L. The temperature for grain growth, although can be selected from among 10 to 90°C, is preferably in the range of 30 to 80°C.

The total addition amount of crystal habit-controlling agent is preferably  $6 \times 10^{-5}$  mol or more, more preferably in the range of  $3 \times 10^{-4}$  to  $6 \times 10^{-2}$  mol, per mol of silver halides of completed emulsion. The timing of addition of the crystal habit-controlling agent can be at any stage from the silver halide grain nucleation to physical ripening and during the grain growth. After the addition, the formation of (111) faces is started. Although the crystal habit-controlling agent may be placed in the reaction vessel in advance, in the formation of tabular grains of small size, it is preferred that the crystal habit-controlling agent be placed in the reaction vessel simultaneously with the grain growth so that the

concentration thereof is increased.

When the amount of dispersion medium used at nucleation is short in growth, it is needed to compensate for the same by an addition. It is  
5 preferred that 10 to 100 g/L of gelatin be present for growth. The compensatory gelatin is preferably gelatin phthalate or gelatin trimellitate.

The pH at grain formation, although arbitrary, is preferably in the neutral to acid region.

10 Now, the (100) tabular grains will be described. The (100) tabular grains are tabular grains having (100) faces as main planes. The shape of these main planes is, for example, a right-angled parallelogram, or a tri- to pentagon corresponding to a right-angled  
15 parallelogram having one corner selected from the four corners of which has been deleted (deletion having the shape of a right-angled triangle composed of the corner apex and sides making the corner), or a tetra- to  
20 octagon corresponding to a right-angled parallelogram having two to four corners selected from the four corners of which have been deleted.

When a right-angled parallelogram having been compensated for the deletions is referred to as a compensated tetragon, the neighboring side ratio  
25 (length of long side/length of short side) of the right-angled parallelogram or compensated tetragon is in the range of 1 to 6, preferably 1 to 4, and more

preferably 1 to 2.

The formation of tabular silver halide emulsion grains having (100) main planes is performed by adding an aqueous solution of silver salt and an aqueous solution of halide to a dispersion medium such as an aqueous solution of gelatin under agitation and mixing them together. For example, JP-A's-6-301129, 6-347929, 9-34045 and 9-96881 disclose such a method that, at the formation, making silver iodide or iodide ions, or silver bromide or bromide ions, exist to thereby produce strain in nuclei due to a difference in size of crystal lattice from silver chloride so that a crystal defect imparting anisotropic growability, such as spiral dislocation, is introduced. When the spiral dislocation is introduced, the formation of two-dimensional nuclei at the surface is not rate-determining under low supersaturation conditions with the result that the crystallization at the surface is advanced. Thus, the introduction of spiral dislocation leads to the formation of tabular grains. Herein, the low supersaturation conditions preferably refer to 35% or less, more preferably 2 to 20%, of the critical addition. Although the crystal defect has not been ascertained as being a spiral dislocation, it is contemplated that the possibility of spiral dislocation is high from the viewpoint of the direction of dislocation introduction and the impartation of

anisotropic growability to grains. It is disclosed in JP-A's-8-122954 and 9-189977 that, for reducing the thickness of tabular grains, retention of the introduced dislocation is preferred.

5           Moreover, the method of forming the (100) tabular grains by adding a (100) face formation accelerator is disclosed in JP-A-6-347928, in which use is made of imidazoles and 3,5-diaminotriazoles, and JP-A-8-339044, in which use is made of polyvinyl alcohols. However,  
10           the present invention is in no way limited thereto.

          Although the grains of high silver chloride content refer to those having a silver chloride content of 80 mol% or more, it is preferred that 95 mol% or more thereof consist of silver chloride. The grains of  
15           the present invention preferably have a so-termed core/shell structure consisting of a core portion and a shell portion surrounding the core portion. Preferably, 90 mol% or more of the core portion consists of silver chloride. The core portion may  
20           further consist of two or more portions whose halogen compositions are different from each other. The volume of the shell portion is preferably 50% or less, more preferably 20% or less, of the total grain volume. The silver halide composition of the shell portion is  
25           preferably silver iodochloride or silver iodobromochloride. The shell portion preferably contains 0.5 to 13 mol%, more preferably 1 to 13 mol%,

of iodide. The silver iodide content of a whole grain is preferably 5 mol% or less, more preferably 1 mol% or less.

Also, it is preferred that the silver bromide  
5 content be higher in the shell portion than in the core portion. The silver bromide content of a whole grain is preferably 20 mol% or less, more preferably 5 mol% or less.

The average grain size (equivalent sphere diameter  
10 in terms of volume) of silver halide grains, although not particularly limited, is preferably in the range of 0.1 to 0.8  $\mu\text{m}$ , more preferably 0.1 to 0.6  $\mu\text{m}$ .

The tabular grains of silver halides preferably  
have an projected area diameter of 0.2 to 1.0  $\mu\text{m}$ .  
15 Herein, the projected area diameter of silver halide grains refers to the diameter of a circle having the same area as the projected area diameter of each individual grain in an electron micrograph. The  
thickness of silver halide grains is preferably 0.2  $\mu\text{m}$   
20 or less, more preferably 0.1  $\mu\text{m}$  or less, and most preferably 0.06  $\mu\text{m}$  or less. In the present invention, 50% or more, in terms of a ratio to total projected area of all the grains, are occupied by silver halide grains having an aspect ratio (ratio of grain  
25 diameter/thickness) of 2 or more, preferably ranging from 5 to 20.

Generally, the tabular grains are of a tabular

shape having two parallel surfaces. Therefore, the "thickness" of the present invention is expressed by the spacing of two parallel surfaces constituting the tabular grains.

5           The grain size distribution of silver halide grains of the present invention, although may be polydisperse or monodisperse, is preferably monodisperse. In particular, the variation coefficient of equivalent circle diameter of tabular grains  
10           occupying 50% or more of the total projected area is preferably 20% or less, ideally 0%.

          When the crystal habit-controlling agent is present on the grain surface after the grain formation, it exerts influence on the adsorption of sensitizing  
15           dye and the development. Therefore, it is preferred to remove the crystal habit-controlling agent after the grain formation. However, when the crystal habit-controlling agent is removed, it is difficult for the  
20           (111) tabular grains of high silver chloride content to maintain the (111) faces under ordinary conditions. Therefore, it is preferable to retain the grain configuration by substitution with a photographically useful compound such as a sensitizing dye. This method is described in, for example, JP-A's-9-80656 and  
25           9-106026, and U.S.P. Nos. 5,221,602, 5,286,452, 5,298,387, 5,298,388 and 5,176,992.

          The crystal habit-controlling agent is desorbed



from grains by the above method. The desorbed crystal habit-controlling agent is preferably removed out of the emulsion by washing. The washing can be performed at such temperatures that the gelatin generally used as  
5 a protective colloid is not solidified. For the washing, use can be made of various known techniques such as the flocculation method and the ultrafiltration method. The washing temperature is preferably 40°C or higher.

10 The desorption of the crystal habit-controlling agent from grains is accelerated at low pH values. Therefore, the pH of the washing step is preferably lowered as far as excess aggregation of grains does not occur.

15 The silver halide emulsion may be provided with additional characteristics depending on the layer in which the emulsion is to be used. Especially when the emulsion is used in a blue sensitive layer, silver halide grains contained in the silver halide emulsion  
20 preferably has a silver iodide content of 3 mol% or more, more preferably 5 mol% or more. Further, when the emulsion is used in a high-speed layer, the projected area diameter is preferably 1  $\mu\text{m}$  or more, and more preferably 2  $\mu\text{m}$  or more.

25 Further, in order to provide the sensitive material of the invention with pressure resistance, the silver halide emulsion may have the following

characteristics. The silver halide emulsion comprising silver halide grains having no dislocation lines in a area within 50%, preferably 80%, from the center of the main plane, when observed with a transmission electron  
5 microscope, in an amount of preferably 80% or more, more preferably 90% or more of all the grains. The center of the main plane means the center of gravity in the area of the main plane.

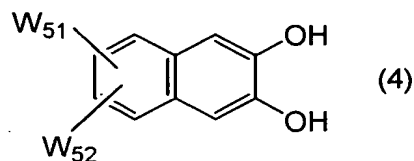
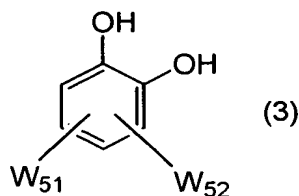
The emulsion used in the invention in general will  
10 be explained below.

Reduction sensitization preferable performed in the present invention can be selected from a method of adding reduction sensitizers to a silver halide emulsion, a method called silver ripening in which  
15 grains are grown or ripened in a low-pAg ambient at pAg 1 to 7, and a method called high-pH ripening in which grains are grown or ripened in a high-pH ambient at pH 8 to 11. It is also possible to combine two or more of these methods.

The method of adding reduction sensitizers is  
20 preferred in that the level of reduction sensitization can be finely adjusted.

As examples of the reduction sensitizer stannous chloride, ascorbic acid and its derivatives,  
25 hydroquinone and its derivatives, catechol and its derivatives, hydroxylamine and its derivatives, amines and polyamines, hydrazine and its derivatives,

para-phenylenediamin and its derivatives,  
 formamidinesulfinic acid(thiourea dioxide), a silane  
 compound, and a borane compound, can be mentioned.  
 In reduction sensitization of the present invention, it  
 is possible to selectively use these reduction  
 sensitizers or to use two or more types of compounds  
 together. Regarding the methods for performing the  
 reduction sensitization, those disclosed in U.S.P.  
 Nos. 2,518,698, 3,201,254, 3,411,917, 3,779,777,  
 3,930,867, may be used. Regarding the methods for  
 using the reduction sensitizer, those disclosed in  
 JP-B's-57-33572 and 58-1410, JP-A-57-179835, may be  
 used. Preferable compounds as the reduction sensitizer  
 are catechol and its derivatives, hydroxylamine and its  
 derivatives, and formamidinesulfinic acid(thiourea  
 dioxide). In performing reduction sensitization, a  
 compound represented by general formula (3) or general  
 formula (4) is preferably used:



In formulas (3) and (4), each of W<sub>51</sub> and  
 W<sub>52</sub> represents a sulfo group or a hydrogen atom.  
 Provided that at least one of W<sub>51</sub> and W<sub>52</sub> represents  
 a sulfo group. A sulfo group is generally an alkali  
 metal salt such as sodium or potassium, or a water-  
 soluble salt such as ammonium salt. Practical examples

of preferable compounds are 3,5-disulfocatecholdisodium salt, 4-sulfocatecholammonium salt, 2,3-dihydroxy-7-sulfonaphthalenesodium salt, and 2,3-dihydroxy-6,7-disulfonaphthalenepotassium salt.

5           Although the addition amount of reduction sensitizers must be so selected as to meet the emulsion manufacturing conditions, a proper amount is  $10^{-7}$  to  $10^{-1}$  mol per mol of a silver halide. The reduction sensitiz-  
10           er is added during grain formation by dissolving thereof to water, or organic solvents such as alcohols, glycols, ketones, esters, and amides.

          Examples of the silver halide solvents which can be employed in the present invention include (a) organic thioethers described in U.S.P. Nos. 3,271,157,  
15           3,531,289, and 3,574,628, JP-A's-54-1019 and 54-158917, (b) thiourea derivatives described in, for example, JP-A's-53-82408, 55-77737 and 55-2982, (c) silver  
          halide solvents having a thiocarbonyl group interposed between an oxygen or sulfur atom and a nitrogen atom,  
20           described in JP-A-53-144319, (d) imidazoles described in JP-A-54-100717, (e) sulfites and (f) thiocyanates.

          Thiocyanates, ammonia and tetramethylthiourea can be mentioned as especially preferred silver halide solvents. The amount of added solvent, although  
25           varied depending on the type thereof, is, if thiocyanate is use, preferably in the range of  $1 \times 10^{-4}$  to  $1 \times 10^{-2}$  mol per mol of silver halide.

It is preferable to make salt of metal ion exist, for example, during grain formation, desalting, or chemical sensitization, or before coating in accordance with the intended use. The metal ion salt is

5 preferably added during grain formation when doped into grains, and after grain formation and before completion of chemical sensitization when used to decorate the grain surface or used as a chemical sensitizer. The salt can be doped in any of an overall grain, only the

10 core, the shell, or the epitaxial portion of a grain, and only a substrate grain. Examples of the metal are Mg, Ca, Sr, Ba, Al, Sc, Y, La, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Ru, Rh, Pd, Re, Os, Ir, Pt, Au, Cd, Hg, Tl, In, Sn, Pb, and Bi. These metals can be added as long as

15 they are in the form of salt that can be dissolved during grain formation, such as ammonium salt, acetate, nitrate, sulfate, phosphate, hydroxide, 6-coordinated complex salt, or 4-coordinated complex salt. Examples are  $\text{CdBr}_2$ ,  $\text{CdCl}_2$ ,  $\text{Cd}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Pb}(\text{CH}_3\text{COO})_2$ ,

20  $\text{K}_3[\text{Fe}(\text{CN})_6]$ ,  $(\text{NH}_4)_4[\text{Fe}(\text{CN})_6]$ ,  $\text{K}_3\text{IrCl}_6$ ,  $(\text{NH}_4)_3\text{RhCl}_6$ , and  $\text{K}_4\text{Ru}(\text{CN})_6$ . The ligand of a coordination compound can be selected from halo, aquo, cyano, cyanate, thiocyanate, nitrosyl, thionitrosyl, oxo, and carbonyl. These metal compounds can be used either singly or in

25 the form of a combination of two or more types of them.

The metal compounds are preferably dissolved in an appropriate solvent, such as water, methanol or

acetone, and added in the form of a solution. To stabilize the solution, an aqueous hydrogen halogenide solution (e.g., HCl or HBr) or an alkali halide (e.g., KCl, NaCl, KBr, or NaBr) can be added. It is also possible to add acid or alkali if necessary. The metal compounds can be added to a reactor vessel either before or during grain formation. Alternatively, the metal compounds can be added to a water-soluble silver salt (e.g., AgNO<sub>3</sub>) or an aqueous alkali halide solution (e.g., NaCl, KBr, or KI) and added in the form of a solution continuously during formation of silver halide grains. Furthermore, a solution of the metal compounds can be prepared independently of a water-soluble salt or an alkali halide and added continuously at a proper timing during grain formation. It is also possible to combine several different addition methods.

It is sometimes useful to perform a method of adding a chalcogen compound during preparation of an emulsion, such as described in U.S.P. No. 3,772,031. In addition to S, Se and Te, cyanate, thiocyanate, selenocyanate, carbonate, phosphate, or acetate may be present.

In the formation of silver halide grains of the present invention, at least one of chalcogen sensitization including sulfur sensitization, selenium sensitization, and tellurium sensitization, noble metal sensitization including gold sensitization and

palladium sensitization, and reduction sensitization can be performed at any point during the process of manufacturing a silver halide emulsion. The use of two or more different sensitizing methods is  
5 preferable. Several different types of emulsions can be prepared by changing the timing at which the chemical sensitization is performed. The emulsion types are classified into: a type in which a chemical sensitization nucleus is embedded inside a grain, a  
10 type in which it is embedded in a shallow position from the surface of a grain, and a type in which it is formed on the surface of a grain. In emulsions of the present invention, the position of a chemical sensitization speck can be selected in accordance with  
15 the intended use. However, it is preferable to form at least one type of a chemical sensitization nucleus in the vicinity of the surface.

One chemical sensitization which can be preferably performed in the present invention is chalcogen  
20 sensitization, noble metal sensitization, or a combination of these. The sensitization can be performed by using active gelatin as described in T.H. James, The Theory of the Photographic Process, 4th ed., Macmillan, 1977, pages 67 to 76. The sensitization can  
25 also be performed by using any of sulfur, selenium, tellurium, gold, platinum, palladium, and iridium, or by using a combination of a plurality of

these sensitizers at pAg 5 to 10, pH 5 to 8, and a temperature of 30°C to 80°C, as described in Research Disclosure, Vol. 120, April, 1974, 12008, Research Disclosure, Vol. 34, June, 1975, 13452, 5 U.S.P.'s 2,642,361, 3,297,446, 3,772,031, 3,857,711, 3,901,714, 4,266,018, and 3,904,415, and British Patent 1,315,755. In the noble metal sensitization, salts of noble metals, such as gold, platinum, palladium, and iridium, can be used. In particular, 10 gold sensitization, palladium sensitization, or a combination of the both is preferred.

In the gold sensitization, gold salts described, for example, in Chimie et Physique Photographique (P. Grafkides, Paul Momtel, 1987, 5th ed.), and Research 15 Disclosure, vol. 307, Item 307105, can be used.

Specifically, in addition to chloroauric acid, potassium chloroaurate, and potassium auriothiocyanate, gold compounds can also be used, e.g., those disclosed in U.S.P. Nos. 2,642,361 (e.g., gold sulfide and gold 20 selenide), 3,503,749 [e.g., gold thiolate having a water-soluble group], 5,049,484

(bis(methylhydantoinato) gold complex), 5,049,485

(mesoionic thiolate gold complexes, e.g., 1,4,5-trimethyl-1,2,4-triazolium-3-thiolate gold complex),

25 5,252,455 and 5,391,727 (macroheterocyclic gold complexes), 5,620,841, 5,700,631, 5,759,760, 5,759,761, 5,912,111, 5,912,112 and 5,939,245, JP-A's-1-147537, 8-



69074, 8-69075 and 9-269554, JP-B-45-29274, German Patent DD-264524A, 264525A, 265474A and 298321A, JP-A's-2001-75214, 2001-75215, 2001-75216, 2001-75217 and 2001-75218.

5           A palladium compound means a divalent or tetravalent salt of palladium. A preferable palladium compound is represented by  $R_2PdX_6$  or  $R_2PdX_4$  wherein R represents a hydrogen atom, an alkali metal atom, or an ammonium group and X represents a halogen atom, e.g., a  
10           chlorine, bromine, or iodine atom.

          More specifically, the palladium compound is preferably  $K_2PdCl_4$ ,  $(NH_4)_2PdCl_6$ ,  $Na_2PdCl_4$ ,  $(NH_4)_2PdCl_4$ ,  $Li_2PdCl_4$ ,  $Na_2PdCl_6$ , or  $K_2PdBr_4$ . It is preferable that  
15           the gold compound and the palladium compound be used in combination with thiocyanate or selenocyanate.

          For the sulfur sensitization, unstable sulfur compounds are used as described in, for example, P. Grafkides, Chimie et Physique Photographique, 5th Ed., Paul Montel, 1987, and Research Disclosure, Vol. 307,  
20           No. 307105.

          Specifically, thiosulfates (e.g., hypo), thioureas (e.g., diphenylthiourea, triethylthiourea, N-ethyl-N'-(4-methyl-2-thiazolyl) thiourea, dicarboxymethyl-dimethylthiourea and carboxymethyl-trimethylthiourea),  
25           thioamides (e.g., thioacetamide), rhodanines (e.g., diethylrhodanine and 5-benzylidene-N-ethylrhodanine), phosphine sulfides (e.g., trimethylphosphine sulfide),

thiohydantoins, 4-oxo-oxazolidine-2-thiones, di- or  
poly-sulfides (e.g., dimorpholine disulfide, cystine,  
and hexathionic acid), mercapto compounds (e.g.,  
cysteine), polythionates, and elemental sulfur as well  
5 as active gelatin. Particularly, thiosulfates,  
thioureas, phosphine sulfides and rhodanines are  
preferred.

For the selenium sensitization, unstable  
selenium compounds are used as described in, for  
10 example, JP-B's-43-13489 and 44-15748, JP-A's-4-25832,  
4-109340, 4-271341, 5-40324, 5-11385, 6-51415, 6-180478,  
6-180478, 6-208186, 6-208184, 6-317867, 7-92599,  
7-98483 and 7-140539.

Specific example thereof include colloidal  
15 metallic selenium, selenoureas (e.g.,  
N,N-dimethylselenourea, trifluoromethylcarbonyl-  
trimethylselenourea, and acetyl-trimethylselenourea),  
selenoamides (e.g., selenoamide and  
N,N-diethylphenylselenoamide), phosphine selenides  
20 (e.g., triphenylphosphine selenide and  
pentafluorophenyl-triphenylphosphine selenide),  
selenophosphates (e.g., tri-p-tolylselenophosphate and  
tri-n-butylselenophosphate), selenoketones (e.g.,  
selenobenzophenone), isoselenocyanates,  
25 selenocarboxylic acids, selenoesters (e.g.,  
methoxyphenylselenocarboxy-2,2-dimethoxycyclohexane  
ester) and diacylselenides. Also useful are

non-unstable selenium compounds as described in JP-B's-46-4553 and 52-34492, for example, selenites, selenocyanic acids (e.g., potassium selenocyanide), selenazoles, and selenides. Particularly, phosphine  
5 selenides, selenoureas, selenoesters and selenocyanic acids are preferred.

For the tellurium sensitization, a unstable tellurium compound is used and the unstable tellurium compounds described in JP-A's-4-224595, 4-271341,  
10 4-333043, 5-303157, 6-27573, 6-180478, 6-208186, 6-208184, 6-317867 and 7-140539 may be used.

Specific examples thereof include phosphine tellurides (e.g., butyl-diisopropylphosphine telluride, tributylphosphine telluride, tributoxyphosphine  
15 telluride, ethoxy-diphenylphosphine telluride), diacyl (di)tellurides (e.g., bis(diphenylcarbamoyl) ditelluride, bis(N-phenyl-N-methylcarbamoyl) ditelluride, bis(N-phenyl-N-methylcarbamoyl) telluride, bis(N-phenyl-N-benzylcarbamoyl) telluride,  
20 bis-(ethoxycarbonyl)telluride), telluroureas (e.g., N,N'-dimethylethylenetellurourea and N,N'-dephenylethylenetellurourea), telluroamides and telluroesters.

As a useful chemical sensitization auxiliary, a  
25 compound is used that is known to suppress fogging and to increase the sensitivity in the process of chemical sensitization, such as azaindenes, azapyridazines and

azapyrimidines. Examples of the chemical sensitization auxiliary modifier will be described in U.S.P. Nos. 2,131,038, 3,411,914 and 3,554,757, JP-A-58-126526, and by G. F. Duffin in "Photographic Emulsion Chemistry" mentioned above, pages 138 to 143.

The amount used of the gold sensitizer or the chalcogen sensitizer use in the present invention varies depending on the silver halide grain or chemical sensitization conditions used, however, it may be from  $10^{-8}$  to  $10^{-2}$  mol, preferably approximately from  $10^{-7}$  to  $10^{-3}$  mol, per mol of silver halide.

There is no particular limitation on the conditions of chemical sensitization in the present invention, but pAg is from 6 to 11, preferably from 7 to 10, pH is from 4 to 10, preferably from 5 to 8, and temperature is from 40 to 95°C, preferably from 45 to 85°C.

An oxidizer capable of oxidizing silver is preferably used during the process of producing the emulsion for use in the present invention. The silver oxidizer is a compound having an effect of acting on metallic silver to thereby convert the same to silver ion. A particularly effective compound is one that converts very fine silver grains, formed as a by-product in the step of forming silver halide grains and the step of chemical sensitization, into silver ions. Each silver ion produced may form a silver salt

sparingly soluble in water, such as a silver halide, silver sulfide or silver selenide, or may form a silver salt easily soluble in water, such as silver nitrate. The silver oxidizer may be either an inorganic or an organic substance. Examples of suitable inorganic oxidizers include ozone, hydrogen peroxide and its adducts (e.g.,  $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$ ,  $2\text{NaCO}_3 \cdot 3\text{H}_2\text{O}_2$ ,  $\text{Na}_4\text{P}_2\text{O}_7 \cdot 2\text{H}_2\text{O}_2$  and  $2\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$ ), peroxy acid salts (e.g.,  $\text{K}_2\text{S}_2\text{O}_8$ ,  $\text{K}_2\text{C}_2\text{O}_6$  and  $\text{K}_2\text{P}_2\text{O}_8$ ), peroxy complex compounds (e.g.,  $\text{K}_2[\text{Ti}(\text{O}_2)\text{C}_2\text{O}_4] \cdot 3\text{H}_2\text{O}$ ,  $4\text{K}_2\text{SO}_4 \cdot \text{Ti}(\text{O}_2)\text{OH} \cdot \text{SO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_3[\text{VO}(\text{O}_2)(\text{C}_2\text{H}_4)_2] \cdot 6\text{H}_2\text{O}$ ), permanganates (e.g.,  $\text{KMnO}_4$ ), chromates (e.g.,  $\text{K}_2\text{Cr}_2\text{O}_7$ ) and other oxyacid salts, halogen elements such as iodine and bromine, perhalogenates (e.g., potassium periodate), salts of high-valence metals (e.g., potassium hexacyanoferrate (II)) and thiosulfonates.

Examples of suitable organic oxidizers include quinones such as p-quinone, organic peroxides such as peracetic acid and perbenzoic acid and active halogen releasing compounds (e.g., N-bromosuccinimide, chloramine T and chloramine B).

Oxidizers preferred in the present invention are inorganic oxidizers selected from among ozone, hydrogen peroxide and its adducts, halogen elements and thiosulfonates and organic oxidizers selected from among quinones.

Photographic emulsions used in the present

invention can contain various compounds in order to prevent fog during the preparing process, storage, or photographic processing of a sensitized material, or to stabilize photographic properties. That is, it is possible to add many compounds known as antifoggants or stabilizers, e.g., thiazoles such as benzothiazolium salt, nitroimidazoles, nitrobenzimidazoles, chlorobenzimidazoles, bromobenzimidazoles, mercaptothiazoles, mercaptobenzothiazoles, mercaptobenzimidazoles, mercaptothiadiazoles, aminotriazoles, benzotriazoles, nitrobenzotriazoles, and mercaptotetrazoles (particularly 1-phenyl-5-mercaptotetrazole); mercaptopyrimidines; mercaptotriazines; a thioketo compound such as oxazolinethione; and azaindenes such as triazaindenes, tetrazaindenes (particularly 4-hydroxy-substituted(1,3,3a,7)tetrazaindenes), and pentazaindenes. For example, compounds described in U.S.P. Nos. 3,954,474 and 3,982,947 and JP-B-52-28660 can be used. One preferred compound is described in JP-A-63-212932. Antifoggants and stabilizers can be added at any of several different timings, such as before, during, and after grain formation, during washing with water, during dispersion after the washing, before, during, and after chemical sensitization, and before coating, in accordance with the intended application. The antifoggants

and stabilizers can be added during preparation of an emulsion to achieve their original fog preventing effect and stabilizing effect. In addition, the antifoggants and stabilizers can be used for various purposes of, e.g., controlling the crystal habit of grains, decreasing the grain size, decreasing the solubility of grains, controlling chemical sensitization, and controlling the arrangement of dyes.

The photographic emulsion for use in the present invention is preferably subjected to a spectral sensitization with a methine dye or the like to thereby exert the effects of the present invention. Examples of employed dyes include cyanine dyes, merocyanine dyes, composite cyanine dyes, composite merocyanine dyes, holopolar cyanine dyes, hemicyanine dyes, styryl dyes and hemioxonol dyes. Particularly useful dyes are those belonging to cyanine dyes, merocyanine dyes and composite merocyanine dyes. These dyes may contain any of nuclei commonly used in cyanine dyes as basic heterocyclic nuclei. Examples of such nuclei include a pyrroline nucleus, an oxazoline nucleus, a thiozoline nucleus, a pyrrole nucleus, an oxazole nucleus, a thiazole nucleus, a selenazole nucleus, an imidazole nucleus, a tetrazole nucleus and a pyridine nucleus; nuclei comprising these nuclei fused with alicyclic hydrocarbon rings; and nuclei comprising these nuclei fused with aromatic hydrocarbon rings, such as an

indolenine nucleus, a benzindolenine nucleus, an indole nucleus, a benzoxazole nucleus, a naphthoxazole nucleus, a benzothiazole nucleus, a naphthothiazole nucleus, a benzoselenazole nucleus, a benzimidazole nucleus and a quinoline nucleus. These nuclei may have substituents on carbon atoms thereof.

The merocyanine dye or composite merocyanine dye may have a 5 or 6-membered heterocyclic nucleus such as a pyrazolin-5-one nucleus, a thiohydantoin nucleus, a 2-thioxazolidine-2,4-dione nucleus, a thiazolidine-2,4-dione nucleus, a rhodanine nucleus or a thiobarbituric acid nucleus as a nucleus having a ketomethylene structure.

These spectral sensitizing dyes may be used either individually or in combination. The spectral sensitizing dyes are often used in combination for the purpose of attaining supersensitization. Representative examples thereof are described in U.S.P. No. 2,688,545, U.S.P. No. 2,977,229, U.S.P. No. 3,397,060, U.S.P. No. 3,522,052, U.S.P. No. 3,527,641, U.S.P. No. 3,617,293, U.S.P. No. 3,628,964, U.S.P. No. 3,666,480, U.S.P. No. 3,672,898, U.S.P. No. 3,679,428, U.S.P. No. 3,703,377, U.S.P. No. 3,769,301, U.S.P. No. 3,814,609, U.S.P. No. 3,837,862, U.S.P. No. 4,026,707, GB No. 1,344,281, GB No. 1,507,803, JP-B-43-4936, JP-B-53-12375, JP-A-52-110618 and JP-A-52-109925.



The emulsion of the present invention may be doped with a dye which itself exerts no spectral sensitizing effect or a substance which absorbs substantially none of visible radiation and exhibits supersensitization,  
5 together with the above spectral sensitizing dye.

The doping of the emulsion with the spectral sensitizing dye may be performed at any stage of the process for preparing the emulsion which is known as being useful. Although the doping is most usually  
10 conducted at a stage between the completion of the chemical sensitization and the coating, the spectral sensitizing dye can be added simultaneously with the chemical sensitizer to thereby simultaneously effect the spectral sensitization and the chemical  
15 sensitization as described in U.S.P. No. 3,628,969 and U.S.P. No. 4,225,666. Alternatively, the spectral sensitization can be conducted prior to the chemical sensitization and, also, the spectral sensitizing dye can be added prior to the completion of silver halide  
20 grain precipitation to thereby initiate the spectral sensitization as described in JP-A-58-113928. Further, the above sensitizing dye can be divided prior to addition, that is, part of the sensitizing dye can be added prior to the chemical sensitization with the rest  
25 of the sensitizing dye added after the chemical sensitization as taught in U.S.P. No. 4,225,666. Still further, the spectral sensitizing dye can be added at

any stage during the formation of silver halide grains according to the method disclosed in U.S.P. No. 4,183,756 and other methods.

5       The addition amount of the sensitizing dye is  $4 \times 10^{-6}$  to  $8 \times 10^{-3}$  mol per mol of silver halide.

Next, compounds used for the lightsensitive materials of the present invention will be described.

First, a compound represented by general formula (I) of the present invention is explained.

10       The compound of the present invention represented by general formula (I) may be used in any situation in the preparation of an emulsion and in a process of producing a lightsensitive material, for example, during the grain formation, during a desalting step, during chemical sensitization and before coating. The  
15       compound can also be added separately a plurality of times during these steps. It is preferable that the compound of the present invention is used after being dissolved in any of water, a water-soluble solvent such as methanol and ethanol, and a mixed solvent of these.  
20       In the case of dissolving a compound in water, as for a compound whose solubility increases when the pH is raised or lowered, it can be added after being dissolved by raising or lowering the pH.

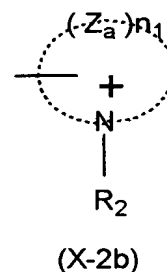
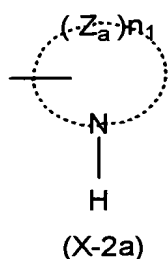
25       The compound of the present invention represented by general formula (I) is preferably used in an emulsion layer, but it is also possible to add the

compound, in advance, to a protective layer or an intermediate layer as well as an emulsion layer, thereby diffusing it. The compound of the present invention may be added either before or after addition  
5 of a sensitizing dye. It is contained in a silver halide emulsion layer in a proportion of preferably from  $1 \times 10^{-9}$  to  $5 \times 10^{-2}$  mol, more preferably from  $1 \times 10^{-8}$  to  $2 \times 10^{-3}$  mol, per mol of silver halide.

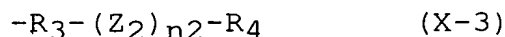
In general formula (I), an adsorbing group to  
10 silver halide represented by X includes groups containing at least one selected from the group consisting of N, S, P, Se and Te, and preferably having a silver ion ligand structure. When k is 2 or more, plural Xs may be the same or different. Examples of  
15 the silver ion ligand structure are as follows:



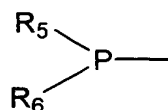
wherein  $G_1$  is a bivalent linking group and represents a bivalent heterocyclic group or a combined bivalent group constituted from a bivalent heterocyclic group and any of a substituted or unsubstituted  
20 alkylene, alkenylene, alkynylene, arylene and  $SO_2$  groups combined with the bivalent heterocyclic group;  $Z_1$  represents a S, Se or Te atom,  $R_1$  represents a hydrogen atom or a counter ion selected from sodium ion, potassium ion, lithium ion and ammonium ion which is  
25 necessary when the ligand structure becomes a dissociated form at  $Z_1$ ;



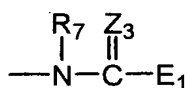
wherein general formulas (X-2a) and (X-2b) each contain a ring whose embodiment includes a 5- to 7-membered, saturated, heterocyclic ring, an unsaturated heterocyclic ring and an unsaturated carbon ring;  $Z_a$  represents an O, N, S, Se or Te atom;  $n_1$  represents an integer of 0 to 3;  $R_2$  represents a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group or an aryl group; when  $n_1$  is 2 or more, plural  $Z_a$ s may be the same or different;



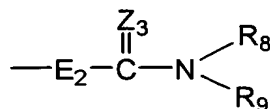
wherein  $Z_2$  represents an S, Se or Te atom,  $n_2$  represents an integer of 1 to 3;  $R_3$  is a bivalent linking group and represents an alkylene group, an alkenylene group, an alkynylene group, an arylene group, a bivalent heterocyclic group, or a combined bivalent group constituted from a bivalent heterocyclic group and any of a substituted or unsubstituted alkylene, alkenylene, alkynylene, arylene and  $SO_2$  groups combined with the bivalent heterocyclic group;  $R_4$  represents an alkyl group, an aryl group or a heterocyclic group; when  $n_2$  is 2 or more, plural  $Z_2$  may be the same or different;



wherein R<sub>5</sub> and R<sub>6</sub> each independently represent an alkyl group, an alkenyl group, an aryl group or a heterocyclic group;

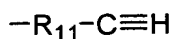


(X-5a)

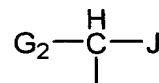


(X-5b)

wherein Z<sub>3</sub> represents a S, Se or Te atom; E<sub>1</sub> represents a hydrogen atom, NH<sub>2</sub>, NHR<sub>10</sub>, N(R<sub>10</sub>)<sub>2</sub>, NHN(R<sub>10</sub>)<sub>2</sub>, OR<sub>10</sub> or SR<sub>10</sub>; E<sub>2</sub> is a bivalent linking group and represents NH, NR<sub>10</sub>, NHNR<sub>10</sub>, O or S; R<sub>7</sub>, R<sub>8</sub> and R<sub>9</sub> each independently represent a hydrogen atom, an alkyl group, an alkenyl group, an aryl group or a heterocyclic group, wherein R<sub>8</sub> and R<sub>9</sub> may be bonded together to form a ring; R<sub>10</sub> represents a hydrogen atom, an alkyl group, an alkenyl group, an aryl group or a heterocyclic group;



(X-6a)



(X-6b)

wherein R<sub>11</sub> is a bivalent linking group and represents an alkylene group, an alkenylene group, an alkynylene group, an arylene group or a bivalent heterocyclic group; G<sub>2</sub> and J each independently represent COOR<sub>12</sub>, SO<sub>2</sub>R<sub>12</sub>, COR<sub>12</sub>, SOR<sub>12</sub>, CN, CHO or NO<sub>2</sub>; R<sub>12</sub> represents an alkyl group, an alkenyl group or an

aryl group.

A detailed description will be made to general formula (X-1). In the formula, examples of the linking group represented by  $G_1$  include a substituted or  
5 unsubstituted, straight chain or branched alkylene group having 1-20 carbon atoms (e.g., methylene, ethylene, trimethylene, propylene, tetramethylene, hexamethylene, 3-oxapentylene and 2-hydroxytrimethylene), a substituted or unsubstituted  
10 cyclic alkylene group having 3-18 carbon atoms (e.g., cyclopropylene, cyclopentylene and cyclohexylene), a substituted or unsubstituted alkenylene group having 2-20 carbon atoms (e.g., ethene and 2-butenylene), a substituted or unsubstituted alkynylene group having 2-  
15 10 carbon atoms (e.g., ethyne), and a substituted or unsubstituted arylene group having 6-20 carbon atoms (e.g., unsubstituted p-phenylene and unsubstituted 2,5-naphthylene).

In that formula, examples of the  $SO_2$  group represented by  $G_1$  include  $-SO_2-$  groups combined with a  
20 substituted or unsubstituted, straight chain or branched alkylene group having 1-10 carbon atoms, a substituted or unsubstituted cyclic alkylene group having 3-6 carbon atoms or an alkenylene group having  
25 2-10 carbon atoms, besides a  $-SO_2-$  group.

Further, examples of the bivalent linking group represented by  $G_1$  include a bivalent heterocyclic group,

or a combined bivalent group constituted from a bivalent heterocyclic group and any of an alkylene, alkenylene, alkynylene, arylene and SO<sub>2</sub> groups combined with the bivalent heterocyclic group, or bivalent groups resulting from benzo-condensation or naphtho-  
condensation of the heterocyclic moieties of the foregoing groups (e.g., 2,3-tetrazolediyl, 1,3-triazolediyl, 1,2-imidazolediyl, 3,5-oxadiazolediyl, 2,4-thiazolediyl, 1,5-benzimidazolediyl, 2,5-benzothiazolediyl, 2,5-benzooxazolediyl, 2,5-pyrimidinediyl, 3-phenyl-2,5-tetrazolediyl, 2,5-pyridinediyl, 2,4-furandiyl, 1,3-piperidinediyl and 2,4-morpholinediyl).

In the above formula, G<sub>1</sub> may have a substituent if possible. Examples of such a substituent are presented below. These substituents are herein called "substituent Y".

Examples of the substituent Y include halogen atom (e.g., a fluorine atom, chlorine atom, and bromine atom), an alkyl group (e.g., methyl, ethyl, isopropyl, n-propyl, and t-butyl), an alkenyl group (e.g., allyl, and 2-butenyl), an alkynyl group (e.g., propargyl), an aralkyl group (e.g., benzyl), an aryl group (e.g., phenyl, naphthyl, and 4-methylphenyl), a heterocyclic group (e.g., pyridyl, furyl, imidazolyl, piperidyl, and morpholino), an alkoxy group (e.g., methoxy, ethoxy, butoxy, 2-ethylhexyloxy, ethoxyethoxy, and

methoxyethoxy), an aryloxy group (e.g., phenoxy and 2-naphthyloxy), an amino group (e.g., unsubstituted amino, dimethylamino, diethyl amino, dipropylamino, ethylamino, and anilino), an acylamino group (e.g., acetyl-  
5 acetyl- and benzoylamino), an ureido group (e.g., unsubstituted ureido, and N-methylureido), an urethane group (e.g., methoxycarbonylamino and phenoxycarbonylamino), a sulfonylamino group (e.g., methylsulfonylamino and phenylsulfonylamino), a  
10 sulfamoyl group (e.g., unsubstituted sulfamoyl, N,N-dimethylsulfamoyl and N-phenylsulfamoyl), a carbamoyl group (e.g., unsubstituted carbamoyl, N,N-diethylcarbamoyl, and N-phenylcarbamoyl), a sulfonyl group (e.g., mesyl and tosyl), a sulfinyl  
15 group (e.g., methylsulfinyl and phenylsulfinyl), an alkyloxycarbonyl group (e.g., methoxycarbonyl and ethoxycarbonyl), an aryloxycarbonyl group (e.g., phenoxycarbonyl), an acyl group (e.g., acetyl, benzoyl, formyl, formyl, and pivaloyl), an acyloxy group (e.g., acetoxy and benzoyloxy), an amide phosphate group (e.g.,  
20 N,N-diethyl amide phosphate), a cyano group, a sulfo group, a thiosulfonic acid group, sulfinic acid group, a carboxy group, a hydroxy group, a phosphono group, a nitro group, an ammonio group, a phosphonio group, a  
25 hydrazino group, and a thiazolino group. If two or more substituents exist, these substituents can be the same or different. These groups can be further



substituted.

Preferable examples of general formula (X-1) will be mentioned below.

In preferable examples of general formula (X-1),  
5 G<sub>1</sub> may be a substituted or unsubstituted arylene group having 6-10 carbon atoms, or a heterocyclic group that forms a 5- to 7-membered ring combined with a substituted or unsubstituted alkylene or arylene group, a benzo-condensed 5- to 7-membered ring, or a naphtho-  
10 condensed 5- to 7-membered ring. S and Se are mentioned as Z<sub>1</sub>, and a hydrogen atom, a sodium ion and a potassium ion are mentioned as R<sub>1</sub>.

More preferably, G<sub>1</sub> is a heterocyclic group which forms a 5- or 6-membered ring combined with a  
15 substituted or unsubstituted arylene group having 6-8 carbon atoms or a benzo-condensed 5- or 6-membered ring, and most preferably is a heterocyclic group which forms a 5- or 6-membered ring combined with an arylene group or a benzo-condensed 5- or 6-membered ring. A further  
20 preferable example of Z<sub>1</sub> is S, and those of R<sub>1</sub> are a hydrogen atom and a sodium ion.

General formulas (X-2a) and (X-2b) will be described in detail.

Examples of the alkyl group, the alkenyl group,  
25 and the alkynyl group represented by R<sub>2</sub> include a substituted or unsubstituted, straight chain or branched alkyl group having 1-10 carbon atoms (e.g.,

methyl, ethyl, isopropyl, n-propyl, n-butyl, t-butyl, 2-pentyl, n-hexyl, n-octyl, t-octyl, 2-ethylhexyl, 2-hydroxyethyl, 1-hydroxyethyl, diethylaminoethyl, n-butoxypropyl and methoxymethyl), a substituted or  
5 unsubstituted, cycloalkyl group having 3-6 carbon atoms (e.g., cyclopropyl, cyclopentyl and cyclohexyl), an alkenyl group having 2-10 carbon atoms (e.g., allyl, 2-butenyl and 3-pentenyl), an alkynyl group having 2-10 carbon atoms (e.g., propargyl and 3-pentynyl), an  
10 aralkyl group having 6-12 carbon atoms (e.g., benzyl), and the like. Examples of the aryl group include a substituted or unsubstituted aryl group having 6-12 carbon atoms (e.g., unsubstituted phenyl and 4-methylphenyl), and the like.

15 The aforementioned  $R_2$  may further have substituent Y, and the like.

Preferable examples of general formulas (X-2a) and (Z-2b) are mentioned below.

In the formula, preferably,  $R_2$  is a hydrogen atom, a substituted or unsubstituted alkyl group having 1-6  
20 carbon atoms, or a substituted or unsubstituted aryl group having 6-10 carbon atoms,  $Z_a$  is O, N or S, and  $n_1$  is an integer of 1 to 3.

More preferably,  $R_2$  is a hydrogen atom or an alkyl  
25 group having 1-4 carbon atoms,  $Z_a$  is N or S, and  $n_1$  is 2 or 3.

Next, general formula (X-3) will be described in

detail.

In the formula, examples of the linking group represented by  $R_3$  include a substituted or unsubstituted, straight chain or branched alkylene group having 1-20 carbon atoms (e.g., methylene, ethylene, trimethylene, isopropylene, tetramethylene, hexamethylene, 3-oxapentylene and 2-hydroxytrimethylene), a substituted or unsubstituted cycloalkylene group having 3-18 carbon atoms (e.g., cyclopropylene, cyclopentynylene and cyclohexylene), a substituted or unsubstituted alkenylene group having 2-20 carbon atoms (e.g., ethene and 2-butenylene), an alkynylene group having 2-10 carbon atoms (e.g., ethyne), and a substituted or unsubstituted arylene group having 6-20 carbon atoms (e.g., unsubstituted p-phenylene and unsubstituted 2,5-naphtylene), an unsubstituted heterocyclic group and heterocyclic groups substituted with an alkylene group, an alkenylene group or an arylene group, and those further substituted with a heterocyclic group (e.g., 2,5-pyridinediyl, 3-phenyl-2,5-pyridinediyl, 1,3-piperidinediyl and 2,4-morpholinediyl).

In that formula, examples of the alkyl group represented by  $R_4$  include a substituted or unsubstituted, straight chain or branched alkyl group having 1-10 carbon atoms (e.g., methyl, ethyl, isopropyl, n-propyl, n-butyl, t-butyl, 2-pentyl, n-

hexyl, n-octyl, t-octyl, 2-ethylhexyl, 2-hydroxyethyl, 1-hydroxyethyl, diethylaminoethyl, dibutylaminoethyl, n-butoxymethyl and methoxymethyl), a substituted or unsubstituted cycloalkyl group having 3-6 carbon atoms (e.g., cyclopropyl, cyclopentyl and cyclohexyl).

Examples of the aryl group include a substituted or unsubstituted aryl group having 6-12 carbon atoms (e.g., unsubstituted phenyl and 2-methylphenyl).

Examples of the heterocyclic group include an unsubstituted heterocyclic group and heterocyclic groups substituted with an alkyl group, an alkenyl group or an aryl group, and those further substituted with a heterocyclic group (e.g., pyridyl, 3-phenylpyridyl, piperidyl and morpholyl).

The aforementioned  $R_4$  may further have substituent Y, and the like.

Preferable examples of general formula (X-3) are mentioned below.

In the formula, preferably,  $R_3$  is a substituted or unsubstituted alkylene group having 1-6 carbon atoms or a substituted or unsubstituted arylene group having 6-10 carbon atoms,  $R_4$  is a substituted or unsubstituted alkyl group having 1-6 carbon atoms or a substituted or unsubstituted aryl group having 6-10 carbon atoms,  $Z_2$  is S or Se, and  $n_2$  is 1 or 2.

More preferably,  $R_3$  is an alkylene group having 1-4 carbon atoms,  $R_4$  is an alkyl group having 1-4 carbon

atoms,  $Z_2$  is S, and  $n_2$  is 1.

Next, general formula (X-4) will be described in detail.

In the formula, examples of the alkyl group and  
5 the alkenyl group represented by  $R_5$  and  $R_6$  include a  
substituted or unsubstituted, straight chain or  
branched alkyl group having 1-10 carbon atoms (e.g.,  
methyl, ethyl, isopropyl, n-propyl, n-butyl, t-butyl,  
2-pentyl, n-hexyl, n-octyl, t-octyl, 2-ethylhexyl,  
10 hydroxymethyl, 2-hydroxyethyl, 1-hydroxyethyl,  
diethylaminoethyl, dibutylaminoethyl, n-butoxymethyl,  
n-butoxypropyl and methoxymethyl), a substituted or  
unsubstituted cycloalkyl group having 3-6 carbon atoms  
(e.g., cyclopropyl, cyclopentyl and cyclohexyl), and an  
15 alkenyl group having 2-10 carbon atoms (e.g., allyl, 2-  
butenyl and 3-pentenyl). Examples of the aryl group  
include a substituted or unsubstituted aryl group  
having 6-12 carbon atoms (e.g., unsubstituted phenyl  
and 4-methylphenyl). Examples of the heterocyclic  
20 group include an unsubstituted heterocyclic group and  
heterocyclic groups substituted with an alkylene group,  
an alkenylene group or an arylene group, and those  
further substituted with a heterocyclic group (e.g.,  
pyridyl, 3-phenylpyridyl, furyl, piperidyl and  
25 morpholyl).

The aforementioned  $R_5$  and  $R_6$  may further have  
substituent Y, and the like.

Preferable examples of general formula (X-4) are mentioned below.

In the formula, preferably,  $R_5$  and  $R_6$  are a substituted or unsubstituted alkyl group having 1-6 carbon atoms or a substituted or unsubstituted aryl group having 6-10 carbon atoms.

More preferably,  $R_5$  and  $R_6$  are an aryl group having 6-8 carbon atoms.

Next, general formulas (X-5a) and (X-5b) will be described in detail.

In the formulas, examples of the group represented by  $E_1$  include  $NH_2$ ,  $NHCH_3$ ,  $NHC_2H_5$ ,  $NHPh$ ,  $N(CH_3)_2$ ,  $N(Ph)_2$ ,  $NHNHC_3H_7$ ,  $NHNHPh$ ,  $OC_4H_9$ ,  $OPh$  and  $SCH_3$ . Examples of the group represented by  $E_2$  include  $NH$ ,  $NCH_3$ ,  $NC_2H_5$ ,  $NPh$ ,  $NHNC_3H_7$  and  $NHNPh$  (here,  $Ph$  = a phenyl group (the same below)).

In general formulas (X-5a) and (X-5b), examples of the alkyl group and the alkenyl group represented by  $R_7$ ,  $R_8$  and  $R_9$  include a substituted or unsubstituted, straight chain or branched alkyl group having 1-10 carbon atoms (e.g., methyl, ethyl, isopropyl, n-propyl, n-butyl, t-butyl, 2-pentyl, n-hexyl, n-octyl, t-octyl, 2-ethylhexyl, hydroxymethyl, 2-hydroxyethyl, 1-hydroxyethyl, diethylaminoethyl, dibutylaminoethyl, n-butoxymethyl, n-butoxypropyl and methoxymethyl), a substituted or unsubstituted cycloalkyl group having 3-6 carbon atoms (e.g., cyclopropyl, cyclopentyl and

cyclohexyl), and an alkenyl group having 2-10 carbon atoms (e.g., allyl, 2-butenyl and 3-pentenyl).

Examples of the aryl group include a substituted or unsubstituted aryl group having 6-12 carbon atoms (e.g.,

5 unsubstituted phenyl and 4-methylphenyl). Examples of

the heterocyclic group include an unsubstituted

heterocyclic group and heterocyclic groups substituted with an alkylene group, an alkenylene group or an

arylene group, and those further substituted with a  
10 heterocyclic group (e.g., pyridyl, 3-phenylpyridyl, furyl, piperidyl and morpholyl).

R<sub>7</sub>, R<sub>8</sub> and R<sub>9</sub> may further have substituent Y, and the like.

Preferable examples of general formulas (X-5a) and  
15 (X-5b) will be mentioned below.

In the formula, preferably, E<sub>1</sub> is an alkyl-substituted or unsubstituted amino group or an alkoxy group. E<sub>2</sub> is an alkyl-substituted or unsubstituted amino-linking group. R<sub>7</sub>, R<sub>8</sub> and R<sub>9</sub> each are a  
20 substituted or unsubstituted alkyl group having 1-6 carbon atoms or a substituted or unsubstituted aryl group having 6-10 carbon atoms. Z<sub>3</sub> is S or Se.

More preferably, E<sub>1</sub> is an alkyl-substituted or unsubstituted amino group, E<sub>2</sub> is an alkyl-substituted  
25 or unsubstituted amino-linking group, R<sub>7</sub>, R<sub>8</sub> and R<sub>9</sub> each are a substituted or unsubstituted alkyl group having 1-4 carbon atoms, and Z<sub>3</sub> is S.

Next, general formulas (X-6a) and (X-6b) will be described in detail.

In the formulas, examples of the groups represented by  $G_2$  and  $J$  include  $\text{COOCH}_3$ ,  $\text{COOC}_3\text{H}_7$ ,  
5  $\text{COOC}_6\text{H}_{13}$ ,  $\text{COOPh}$ ,  $\text{SO}_2\text{CH}_3$ ,  $\text{SO}_2\text{C}_4\text{H}_9$ ,  $\text{COC}_2\text{H}_5$ ,  $\text{COPh}$ ,  $\text{SOCH}_3$ ,  
 $\text{SOPh}$ ,  $\text{CN}$ ,  $\text{CHO}$  and  $\text{NO}_2$ .

In the formulas, examples of the linking group represented by  $R_{11}$  include a substituted or  
unsubstituted, straight chain or branched alkylene  
10 group having 1-20 carbon atoms (e.g., methylene,  
ethylene, trimethylene, propylene, tetramethylene,  
hexamethylene, 3-oxapentylene and 2-  
hydroxytrimethylene), a substituted or unsubstituted  
cycloalkylene group having 3-18 carbon atoms (e.g.,  
15 cyclopropylene, cyclopentylene and cyclohexylene), a  
substituted or unsubstituted alkenylene group having 2-  
20 carbon atoms (e.g., ethene and 2-butenylene), an  
alkynylene group having 2-10 carbon atoms (e.g.,  
ethyne), and a substituted or unsubstituted arylene  
20 group having 6-20 carbon atoms (e.g., unsubstituted p-  
phenylene and unsubstituted 2,5-naphtylene).

Further, examples of the bivalent linking group represented by  $R_{11}$  include a bivalent heterocyclic  
group, or a bivalent group constituted from a bivalent  
25 group and any of an alkylene, alkenylene, alkynylene,  
arylene and  $\text{SO}_2$  groups combined with the bivalent  
heterocyclic group (e.g., 2, 5-pyridinediyl, 3-phenyl-



2,5-pyridinediyl, 2,4-furandiyl, 1,3-piperidinediyl and 2,4-morpholinediyl).

In the formulas,  $R_{11}$  may further have substituent Y, and the like.

5           Preferable examples of general formulas (X-6a) and (X-6b) are mentioned below.

10           In the formula, preferably,  $G_2$  and J are a carboxylic acid ester or carbonyl having 2-6 carbon atoms, and  $R_{11}$  is a substituted or unsubstituted alkylene group having 1-6 carbon atoms or a substituted or unsubstituted arylene group having 6-10 carbon atoms.

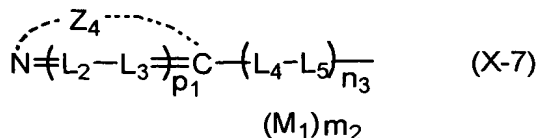
15           More preferably,  $G_2$  and J are a carboxylic acid ester having 2-4 carbon atoms, and  $R_{11}$  is a substituted or unsubstituted alkylene group having 1-4 carbon atoms or a substituted or unsubstituted arylene group having 6-8 carbon atoms.

20           A rank of the preferable general formulas of the silver halide-adsorbing group represented by X is: (X-1) > (X-2a) > (X-2b) > (X-3) > (X-5a) > (X-5b) > (X-4) > (X-6a) > (X-6b).

Next, the light-absorbing group represented by X in general formula (I) will be described in detail.

Examples of the light-adsorbing group represented by X in general formula (I) are as follows:

25



In the formula,  $Z_4$  represents an atomic group necessary for forming a 5- or 6-membered nitrogen-containing heterocycle, and  $L_2$ ,  $L_3$ ,  $L_4$  and  $L_5$  each represent a methine group.  $p_1$  represents 0 or 1, and  
5  $n_3$  represents an integer of 0 to 3.  $M_1$  represents a counter ion to balance a charge, and  $m_2$  represents an integer of 0 to 10 necessary to neutralize the charge in the molecule. The nitrogen-containing heterocycle that  $Z_4$  forms may have an unsaturated carbon ring, such  
10 as a benzene ring, condensed therewith.

In the formula, examples of the 5- or 6-membered nitrogen-containing heterocycle represented by  $Z_4$  include a thiazolidine nucleus, a thiazole nucleus, a benzothiazole nucleus, an oxazoline nucleus, an oxazole  
15 nucleus, a benzoxazole nucleus, a selenazoline nucleus, a selenazole nucleus, a benzoselenazole nucleus, a 3,3-dialkylindolenine nucleus (e.g., 3,3-dimethylindolenine), an imidazoline nucleus, an imidazole nucleus, a benzimidazole nucleus, a 2-  
20 pyridine nucleus, a 4-pyridine nucleus, a 2-quinoline nucleus, a 4-quinoline nucleus, a 1-isoquinoline nucleus, a 3-isoquinoline nucleus, an imidazo[4,5-b]quinoxaline nucleus, an oxadiazole nucleus, a thiadiazole nucleus, a tetrazole nucleus and a  
25 pyrimidine nucleus.

The 5- or 6-membered nitrogen-containing heterocycle represented by  $Z_4$  may have the

aforementioned substituent Y.

In the formula, L<sub>2</sub>, L<sub>3</sub>, L<sub>4</sub> and L<sub>5</sub> each represent an independent methine group. The methine group represented by L<sub>2</sub>, L<sub>3</sub>, L<sub>4</sub> and L<sub>5</sub> may have a substituent, examples of which include a substituted or unsubstituted alkyl group having 1-15 carbon atoms (e.g., methyl, ethyl and 2-carboxyethyl), a substituted or unsubstituted aryl group having 6-20 carbon atoms (e.g., phenyl and o-carboxyphenyl), a substituted or unsubstituted heterocyclic group having 3-20 carbon atoms (e.g., a monovalent group obtained by removing one hydrogen atom from N,N-diethylbarbituric acid), a halogen atom (e.g., chlorine, bromine, fluorine and iodine), an alkoxy group having 1-15 carbon atoms (e.g., methoxy and ethoxy), an alkylthio group having 1-15 carbon atoms (e.g., methylthio and ethylthio), an arylthio group having 6-20 carbon atoms (e.g., phenylthio), and an amino group having 0-15 carbon atoms (e.g., N,N-diphenylamino, N-methyl-N-phenylamino and N-methylpiperazino).

Further, the substituent may combine any two of L<sub>2</sub> to L<sub>5</sub> to form a ring. In addition, the methine group represented by any of L<sub>2</sub> to L<sub>5</sub> can combine with another site via a substituent to form a ring.

In the formula, M<sub>1</sub> is included in the formula to show the presence or absence of a cation or an anion when a counter ion is necessary for neutralizing an

ionic charge in the light-absorbing group. Typical examples of such a cation include an inorganic cation such as a hydrogen ion ( $H^+$ ) and an alkali metal ion (e.g., a sodium ion, a potassium ion, and a lithium ion), and an organic cation such as an ammonium ion (e.g., an ammonium ion, a tetraalkylammonium ion, a pyridinium ion, and an ethylpyridinium ion). While an anion may be an inorganic or organic one, with examples including a halogen anion (e.g., a fluoride ion, a chloride ion, a bromide ion and an iodide ion), a substituted arylsulfonate ion (e.g., a p-toluenesulfonate ion and a p-chlorobenzenesulfonate ion), an aryldisulfonate ion (e.g., a 1,3-benzenedisulfonate ion, a 1,5-naphthalenedisulfonate ion and a 2,6-naphthalenedisulfonate ion), an alkylsulfate ion (e.g., a methylsulfate ion), a sulfate ion, a thiocyanate ion, a perchlorate ion, a tetrafluoroborate ion, a picrate ion, an acetate ion and a trifluoromethanesulfonate ion. Further, a light-absorbing group having an ionic polymer or reversed charge may be used as the light-absorbing group.

In the formula, a sulfo and carboxy groups will be described as  $SO_3^-$  and  $CO_2^-$ , respectively, but they can be described as  $SO_3H$  and  $CO_2H$  when a counter ion is a hydrogen ion.

In the formula,  $m_2$  represents a number necessary for balancing the charge and when a salt is formed in a

molecule, m2 is 0.

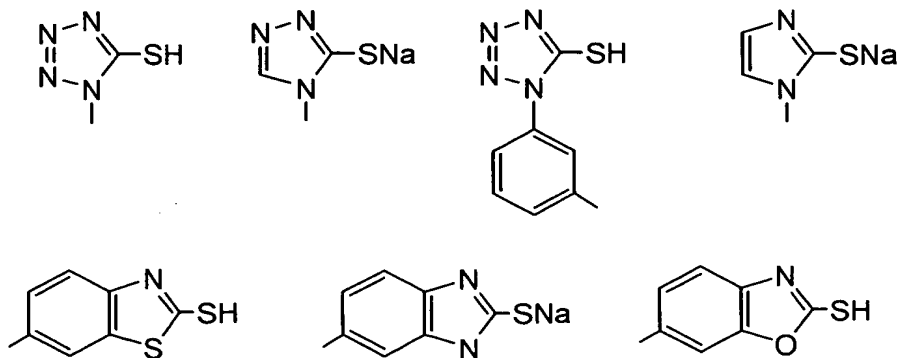
Preferable examples of general formula (X-7) are mentioned below.

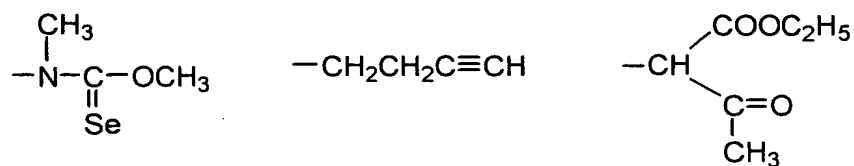
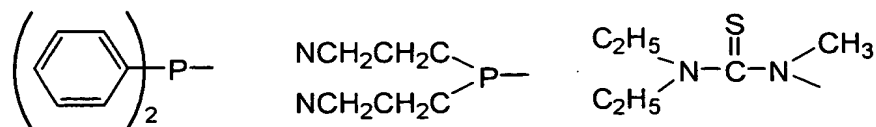
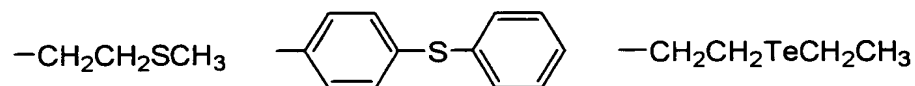
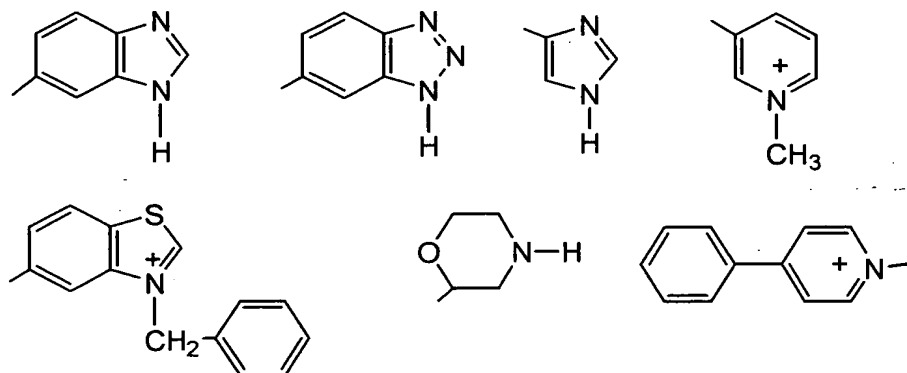
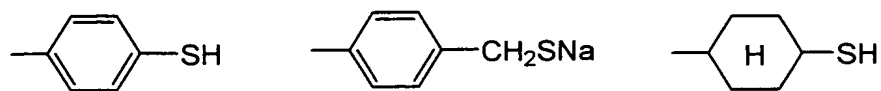
In a preferable general formula (X-7), Z<sub>4</sub> is a  
5 benzoxazole nucleus, a benzothiazole nucleus, a  
benzoimidazole nucleus or a quinoline nucleus. L<sub>2</sub>, L<sub>3</sub>,  
L<sub>4</sub> and L<sub>5</sub> each are an unsubstituted methine group. p<sub>1</sub>  
is 0 and n<sub>3</sub> is 1 or 2.

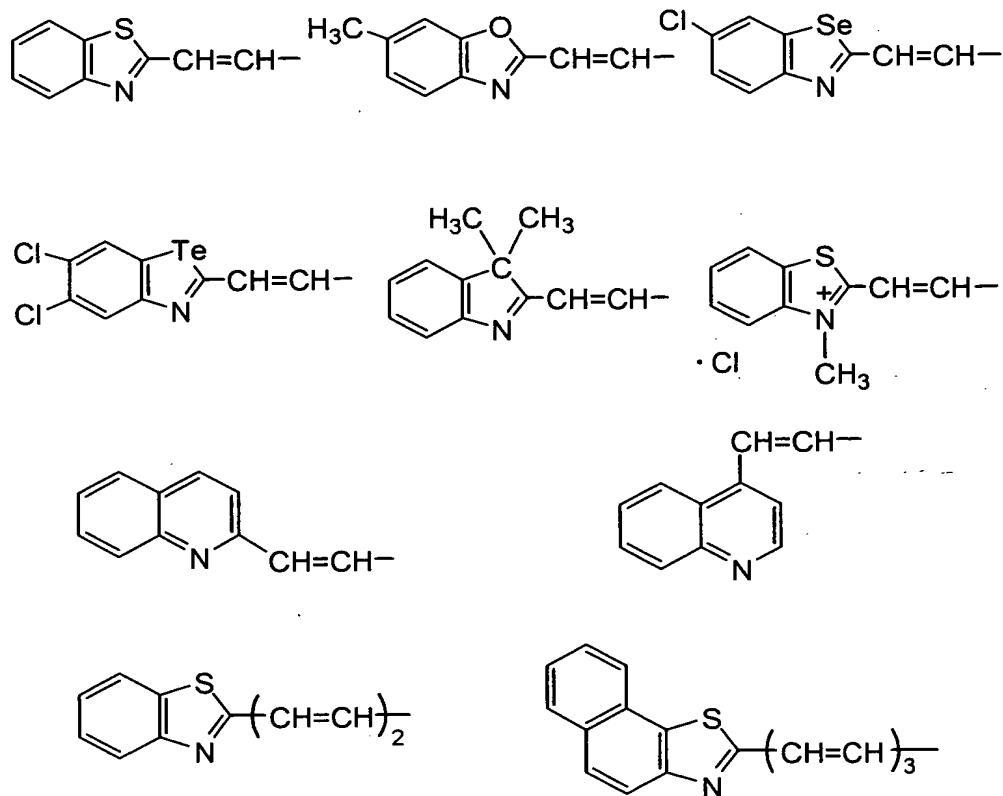
More preferably, Z<sub>4</sub> is a benzoxazole nucleus or a  
10 benzothiazole nucleus, and n<sub>3</sub> is 1. The especially  
preferable Z<sub>4</sub> is a benzothiazole nucleus.

In general formula (I), k is preferably 0 or 1,  
and more preferably 1.

The following are specific examples of X group  
15 used in the present invention, but the compounds to be  
used for the present invention are not restricted to  
them.







Next, a linking group represented by L in general  
 5 formula (I) will be described in detail.

In general formula (I), examples of the linking  
 group represented by L include a substituted or  
 unsubstituted, straight chain or branched alkylene  
 group having 1-20 carbon atoms (e.g., methylene,  
 ethylene, trimethylene, propylene, tetramethylene,  
 10 hexamethylene, 3-oxapentylene and 2-  
 hydroxytrimethylene), a substituted or unsubstituted  
 cycloalkylene group having 3-18 carbon atoms (e.g.,  
 cyclopropylene, cyclopentylene and cyclohexylene),  
 15 a substituted or unsubstituted alkenylene group having  
 2-20 carbon atoms (e.g., ethene and 2-butenylene),  
 an alkynylene group having 2-10 carbon atoms (e.g.,

ethyne), and a substituted or unsubstituted arylene group having 6-20 carbon atoms (e.g., unsubstituted p-phenylene and unsubstituted 2,5-naphtylene), a heterocyclic linking group (e.g., 2,6-pyridinediyl),  
5 a carbonyl group, a thiocarbonyl group, an imide group, a sulfonyl group, a bivalent sulfonic acid group, an ester group, a thioester group, a bivalent amide group, an ether group, a thioether group, a bivalent amino group, a bivalent ureido group, a bivalent thioureido group and a thiosulfonyl group. These linking groups  
10 may be combined to form a new linking group. When m is 2 or more, plural Ls may be the same or different.

L may further have the aforementioned substituent Y, and the like.

15 Preferable examples of the linking group L include an alkylene group having 1-10 carbon atoms resulting from combination of an unsubstituted alkylene group having 1-10 carbon atoms and an amino, amide, thioether, ureido, or sulfonyl group, and more preferably, a an  
20 alkylene group having 1-6 carbon atoms resulting from combination of an unsubstituted alkylene group having 1-6 carbon atoms and an amino, amide or thioether group.

In general formula (I), m is preferably 0 or 1, and more preferably 1.

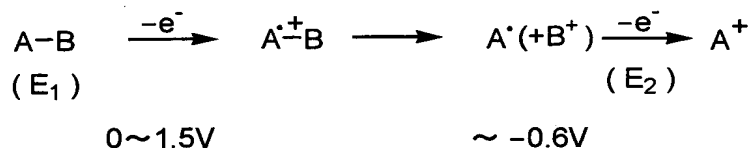
25 Next, electron-donating group A will be described in detail.

There will be described below a reaction process



in which an A-B portion is oxidized or fragmentized to generate an electron, resulting in formation of radical A $\cdot$  and the radical A $\cdot$  is further oxidized to generate an electron and increase sensitivity.

5

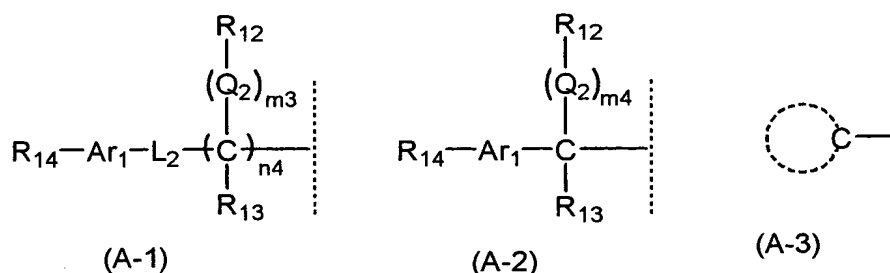


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Since A is an electron-donating group, it is preferable that a substituent, even it has any structure, on the aromatic ring is selected so as to cause A to have excessive electron. For example, it is preferable to adjust the oxidation potential by introducing an electron-donating group when the aromatic ring does not have excessive electron or, conversely, by introducing an electron-withdrawing group when, like anthracene, the aromatic ring has extremely excessive electron.

15

Preferable A group is that having the following general formulas:



20

In general formulas (A-1) and (A-2), R<sub>12</sub> and R<sub>13</sub> each independently represent a hydrogen atom, a substituent or unsubstituted alkyl, aryl, alkylene or arylene group. R<sub>14</sub> represents an alkyl group, COOH,

halogen,  $N(R_{15})_2$ ,  $OR_{15}$ ,  $SR_{15}$ ,  $CHO$ ,  $COR_{15}$ ,  $COOR_{15}$ ,  
 $CONHR_{15}$ ,  $CON(R_{15})_2$ ,  $SO_3R_{15}$ ,  $SO_2NHR_{15}$ ,  $SO_2NR_{15}$ ,  $SO_2R_{15}$ ,  
 $SOR_{15}$  or  $CSR_{15}$ .  $Ar_1$  represents an arylene group or a  
heterocyclic linking group.  $R_{12}$  and  $R_{13}$ , and  $R_{12}$  and  
5  $Ar_1$  each may be combined to form a ring.  $Q_2$  represents  
 $O$ ,  $S$ ,  $Se$  or  $Te$ .  $m_3$  and  $m_4$  each represent 0 or 1.  $n_4$   
represents an integer of 1 to 3.  $L_2$  represents  $N-R$   
(here,  $R$  represents a substituted or unsubstituted  
alkyl group),  $N-Ar$ ,  $O$ ,  $S$  or  $Se$ . The form of the ring  
10 that  $R_{12}$  and  $R_{13}$ , and  $R_{12}$  and  $Ar_1$  form represents a 5-  
to 7-membered heterocyclic or unsaturated ring.  $R_{15}$   
represents a hydrogen atom, an alkyl group or an aryl  
group. The form of ring of general formula (A-3)  
represents a substituted or unsubstituted, 5- to 7-  
15 membered, unsaturated or heterocyclic group.

General formulas (A-1), (A-2) and (A-3) will be  
described in detail.

In the formulas, examples of the alkyl group  
represented by  $R_{12}$  and  $R_{13}$  include a substituted or  
20 unsubstituted, straight chain or branched alkyl group  
having 1-10 carbon atoms (e.g., methyl, ethyl,  
isopropyl, n-propyl, n-butyl, t-butyl, 2-pentyl, n-  
hexyl, n-octyl, t-octyl, 2-ethylhexyl, 2-hydroxyethyl,  
1-hydroxyethyl, diethylaminoethyl, dibutylaminoethyl,  
25 n-butoxymethyl and methoxymethyl), a substituted or  
unsubstituted cycloalkyl group having 3-6 carbon atoms  
(e.g., cyclopropyl, cyclopentyl and cyclohexyl).

Examples of the aryl group include a substituted or unsubstituted aryl group having 6-12 carbon atoms (e.g., unsubstituted phenyl and 2-methylphenyl).

5        Examples of the alkylene group include a substituted or unsubstituted, straight chain or branched alkylene group having 1-10 carbon atoms (e.g., methylene, ethylene, trimethylene, tetramethylene and methoxyethylene), and examples of the arylene group include a substituted or unsubstituted arylene group  
10        having 6-12 carbon atoms (e.g., unsubstituted phenylene, 2-methylphenylene and naphthylene).

      In general formulas (A-1) and (A-2), examples of the group represented by  $R_{14}$  include an alkyl group (e.g., methyl, ethyl, isopropyl, n-propyl, n-butyl, 2-pentyl, n-hexyl, n-octyl, 2-ethylhexyl, 2-hydroxyethyl and n-butoxymethyl), a COOH group, a halogen atom (e.g., a fluorine atom, a chlorine atom and a bromine atom),  
15        OH,  $N(CH_3)_2$ ,  $NPh_2$ ,  $OCH_3$ ,  $OPh$ ,  $SCH_3$ ,  $SPh$ , CHO,  $COCH_3$ ,  $COPh$ ,  $COOC_4H_9$ ,  $COOCH_3$ ,  $CONHC_2H_5$ ,  $CON(CH_3)_2$ ,  $SO_3CH_3$ ,  
20         $SO_3C_3H_7$ ,  $SO_2NHCH_3$ ,  $SO_2N(CH_3)_2$ ,  $SO_2C_2H_5$ ,  $SOCH_3$ ,  $CSPH$  and  $CSCH_3$ .

      Examples of  $Ar_1$  represented by general formulas (A-1) and (A-2) include a substituted or unsubstituted arylene having 6-12 carbon atoms (e.g., phenylene,  
25        2-methylphenylene and naphthylene), and a bivalent or trivalent group obtained by removing one or two hydrogen atoms from a substituted or unsubstituted

heterocyclic group (e.g., pyridyl, 3-phenylpyridyl, piperidyl and morpholyl).

Examples of  $L_2$  represented by general formula (A-1) include  $NH$ ,  $NCH_3$ ,  $NC_4H_9$ ,  $NC_3H_7(i)$ ,  $NPh$ ,  $NPh-CH_3$ ,  
5 O, S, Se and Te.

Examples of the ring form of (A-3) include an unsaturated 5- to 7-membered carbon ring, a saturated or unsaturated 5- to 7-membered heterocycle (e.g.,  
10 furyl, piperidyl and morpholyl).

On  $R_{12}$ ,  $R_{13}$ ,  $R_{14}$ ,  $Ar_1$  and  $L_2$  in general formulas (A-1) and (A-2), and a ring in general formula (A-3) may further have substituent Y, and the like.

Preferable examples of general formulas (A-1), (A-2) and (A-3) are mentioned below.

15 In general formulas (A-1) and (A-2), preferably,  $R_{12}$  and  $R_{13}$  are each a substituted or unsubstituted alkyl group having 1-6 carbon atoms, an alkylene group, or a substituted or unsubstituted aryl group having 6-10 carbon atoms;  $R_{14}$  is a substituted or unsubstituted  
20 alkyl group having 1-6 carbon atoms, an amino group monosubstituted or disubstituted with an alkyl group having 1-4 carbon atoms, a carboxylic acid, halogen or a carboxylic ester having 1-4 carbon atoms;  $Ar_1$  is a substituted or unsubstituted arylene group having 6-10  
25 carbon atoms;  $Q_2$  is O, S or Se;  $m_3$  and  $m_4$  are each 0 or 1;  $n_4$  is 1 to 3; and  $L_2$  is an amino group having 0-3 carbon atoms substituted with an alkyl group.

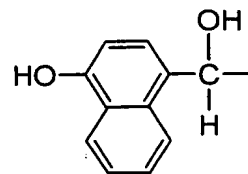
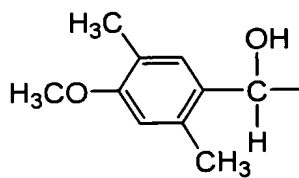
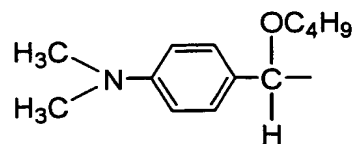
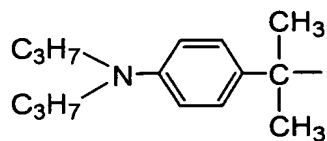
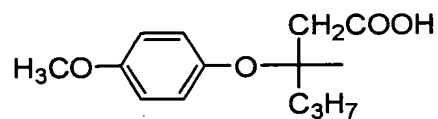
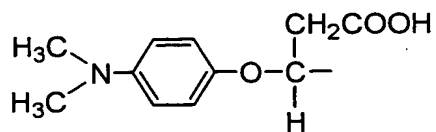
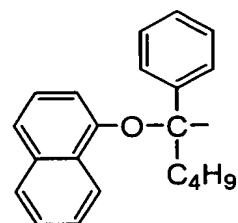
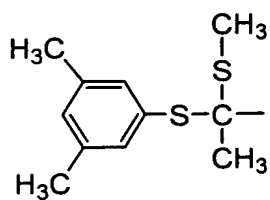
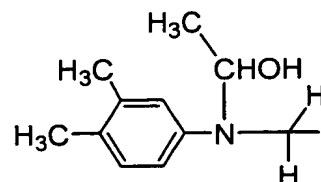
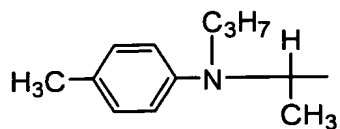
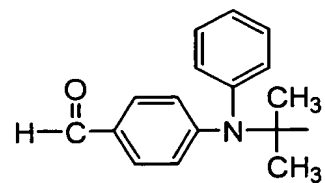
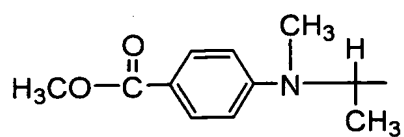
In general formula (A-3), a preferable ring form is a saturated or unsaturated 5- to 7-membered heterocycle.

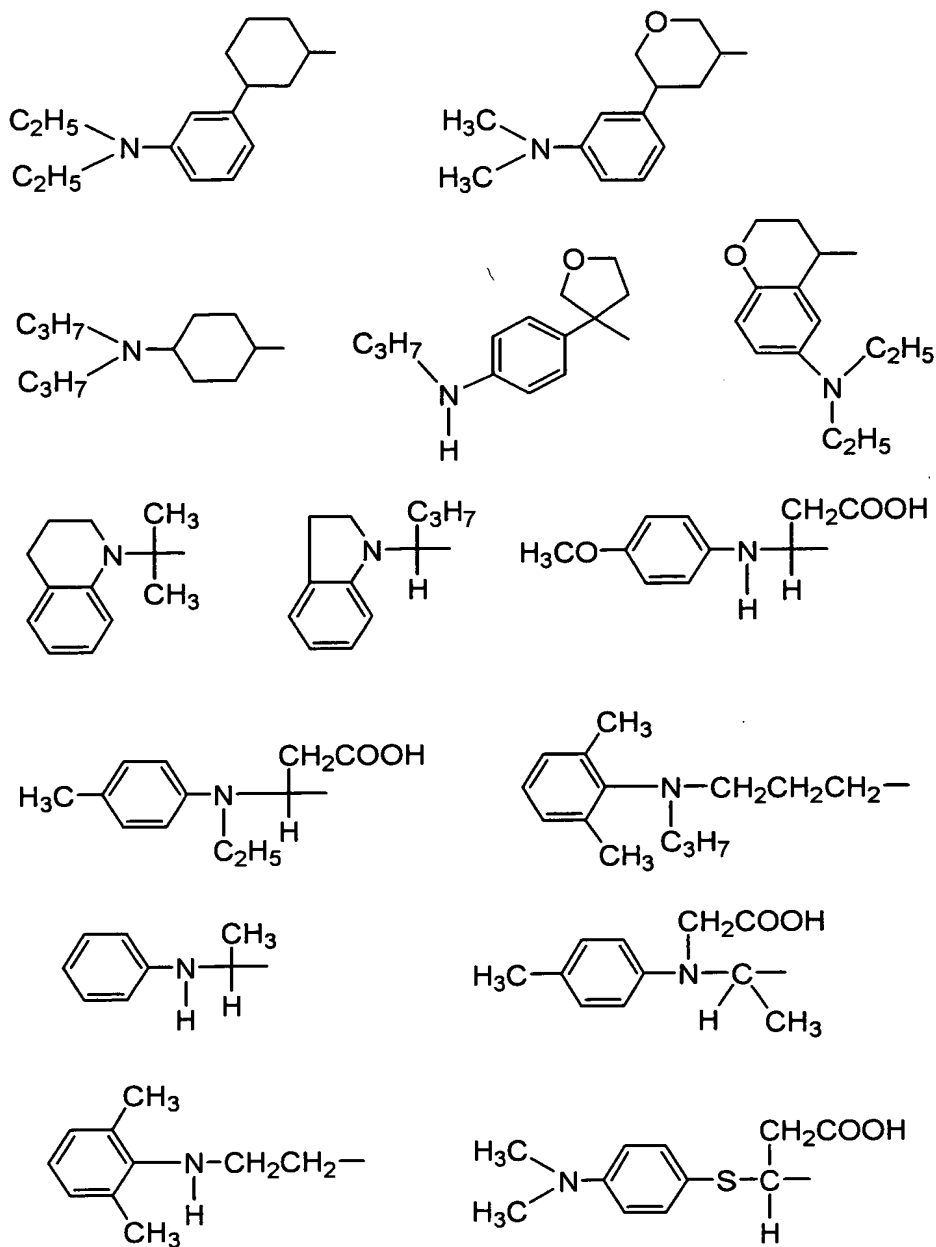
5 In general formulas (A-1) and (A-2), R<sub>12</sub> and R<sub>13</sub> are more preferably a substituted or unsubstituted alkyl group or alkylene group having 1-4 carbon atoms, R<sub>14</sub> is an unsubstituted alkyl group having 1-4 carbon atoms or an alkyl group having 1-4 carbon atoms substituted with monoamino or diamino, Ar<sub>1</sub> is a  
10 substituted or unsubstituted arylene group having 6-10 carbon atoms, Q<sub>2</sub> is O or S, m<sub>3</sub> and m<sub>4</sub> are 0, n<sub>4</sub> is 1, and L<sub>2</sub> is an amino group having 0-3 carbon atoms substituted with an alkyl group.

15 In general formula (A-3), a more preferable ring form is a 5- or 6-membered heterocycle.

The location where group A is combined with group L (group X when m=0) is Ar<sub>1</sub> and R<sub>12</sub> or R<sub>13</sub>.

20 The following are specific examples of group A used in the present invention, but the compounds to be used for the present invention are not restricted to them.





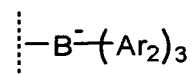
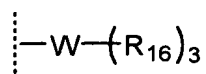
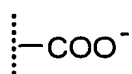
5

Next, group B will be described in detail.

When B is a hydrogen atom, it is oxidized and then deprotonated to generate a radical  $\text{A}\cdot$ .

A preferable group B is one having a hydrogen atom and the following formula.

10



(B-1)

(B-2)

(B-3)

In general formulas (B-1), (B-2) and (B-3), W represents Si, Sn or Ge. R<sub>16</sub> each independently represent an alkyl group, and Ar<sub>2</sub> each independently represent an aryl group.

It is possible to cause general formulas (B-2) and (B-3) to combine with a adsorbing group X.

General formulas (B-1), (B-2) and (B-3) will be described in detail. In the formulas, examples of the alkyl group represented by  $R_{16}$  include a substituted or unsubstituted, straight chain or branched alkyl group having 1-6 carbon atoms (e.g., methyl, ethyl, isopropyl, n-propyl, n-butyl, t-butyl, 2-pentyl, n-hexyl, n-octyl, t-octyl, 2-ethylhexyl, 2-hydroxyethyl, 1-hydroxyethyl, n-butoxyethyl and methoxymethyl), and a substituted or unsubstituted aryl group having 6-12 carbon atoms (e.g., phenyl and 2-methylphenyl).

R<sub>16</sub> and Ar<sub>2</sub> in general formulas (B-2) and (B-3) may further have the aforementioned substituent Y, and the like.

The following are preferable examples of general formulas (B-1), (B-2) and (B-3).

In general formulas (B-2) and (B-3), preferably, R<sub>16</sub> is a substituted or unsubstituted alkyl group having 1-4 carbon atoms, Ar<sub>2</sub> is a substituted or



unsubstituted aryl group having 6-10 carbon atoms, and W is Si or Sn.

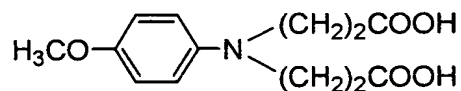
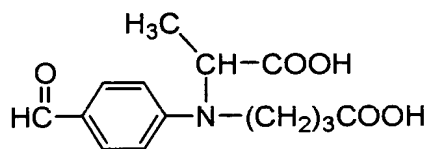
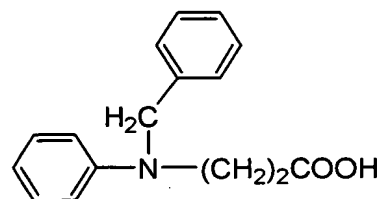
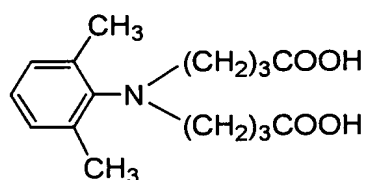
In general formulas (B-2) and (B-3), more preferably,  $R_{16}$  is a substituted or unsubstituted alkyl group having 1-3 carbon atoms,  $Ar_2$  is a substituted or unsubstituted aryl group having 6-8 carbon atoms, and W is Si.

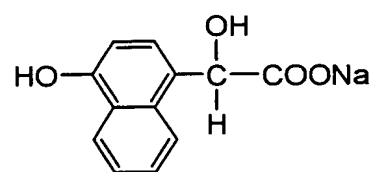
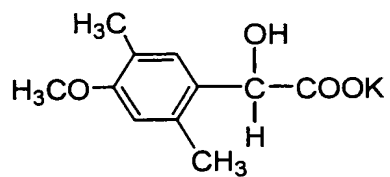
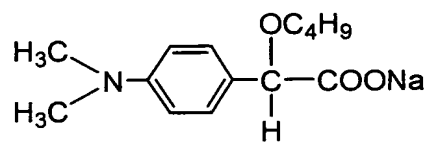
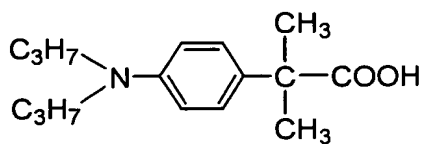
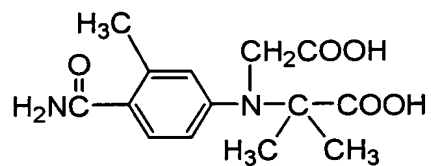
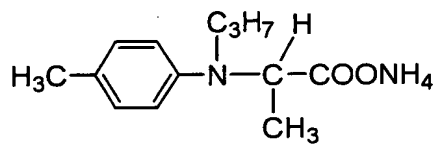
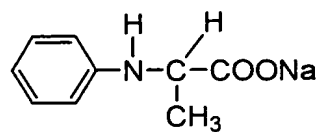
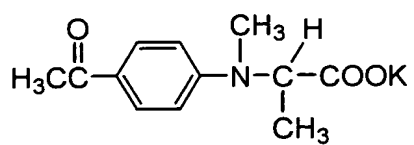
In general formulas (B-1), (B-2) and (B-3), the most preferred are  $COO^-$  of general formula (B-1) and  $Si-(R_{16})_3$ .

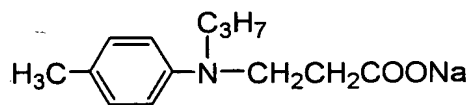
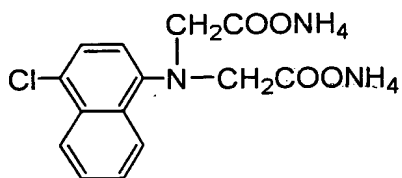
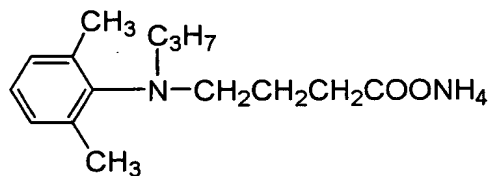
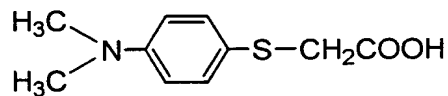
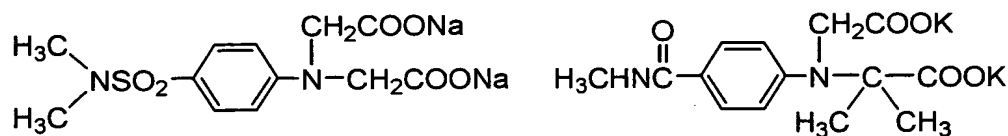
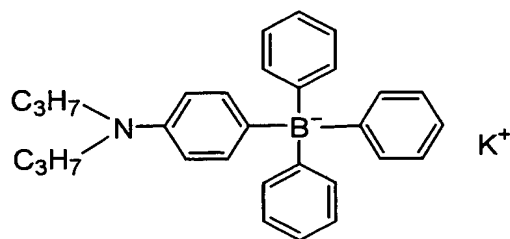
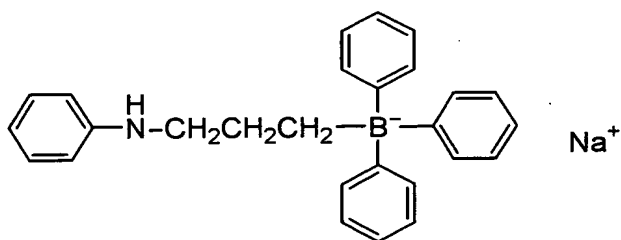
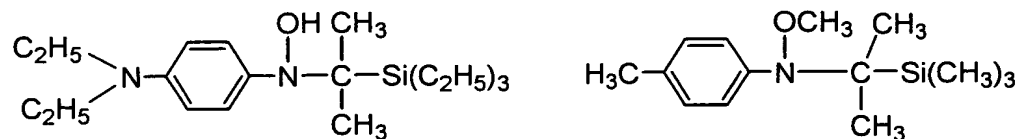
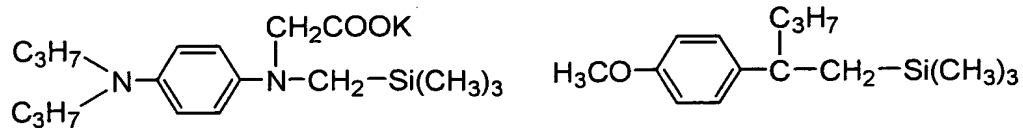
In general formula (I), a preferable n is 1.

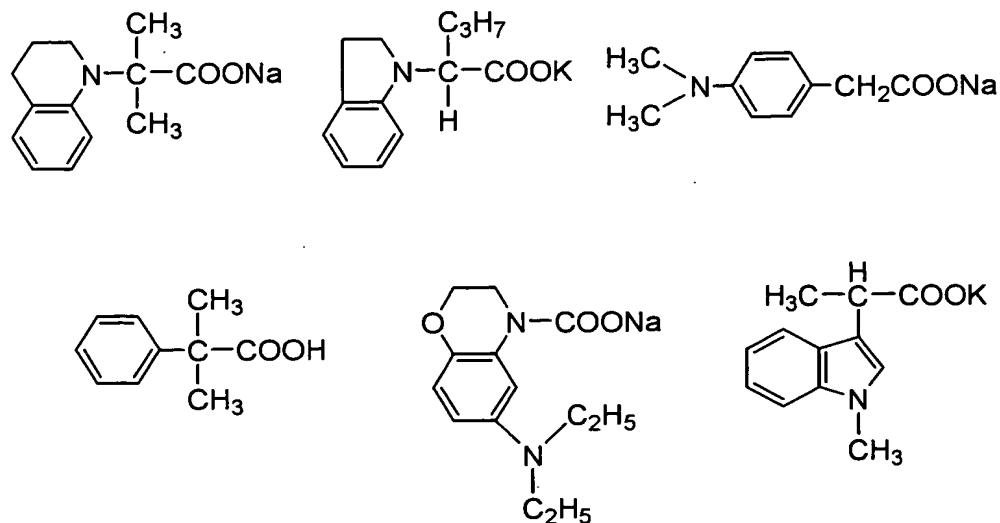
Further, in general formula (I), when n is 2, two (A-B)s may be the same or different.

The following are examples of group (A-B) used in the present invention, but the present invention is not restricted to them.









Examples of the counter ion necessary for balancing the charge of the compound A-B shown above include a sodium ion, a potassium ion, a triethylammonium ion, a diisopropylammonium ion, a tetrabutylammonium ion and a tetramethylguanidinium ion.

A preferable oxidation potential of A-B ranges from 0 to 1.5 V, more preferably from 0 to 1.0 V, and still more preferably from 0.3 to 1.0 V.

A preferable oxidation potential of the radical A $\cdot$  (E<sub>2</sub>) resulting from a bond cleavage reaction ranges from -0.6 to -2.5 V, more preferably from -0.9 to -2V, and still more preferably from -0.9 to -1.6 V.

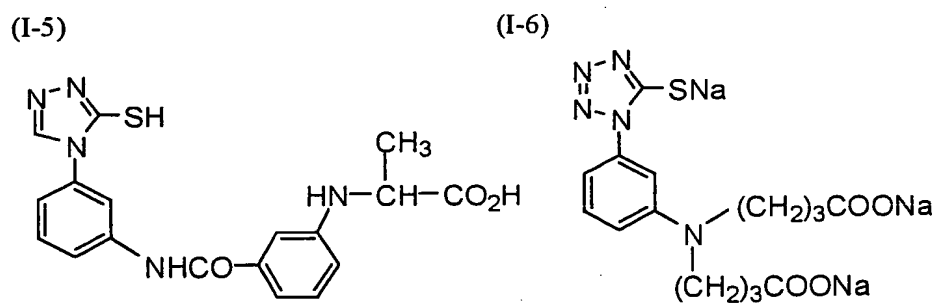
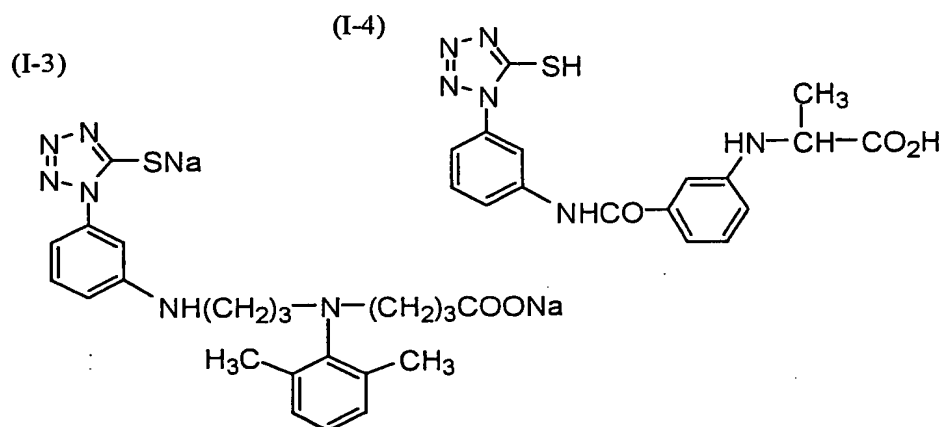
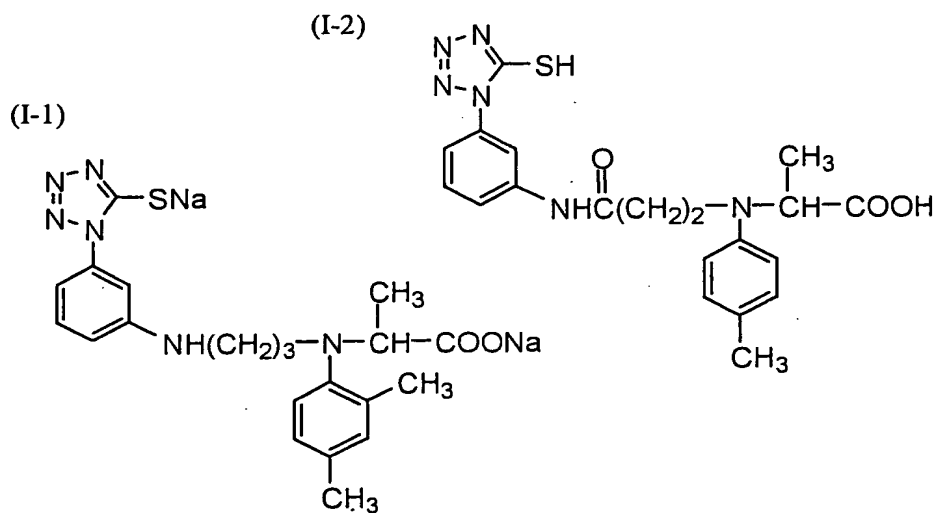
A method for measuring the oxidation potential is as follows.

E1 can be performed by the cyclic voltammetry method. An electron donor A is dissolved in acetonitrile/0.1 M or a water 80%/20% (volume %) solution containing lithium chlorate. A glassy carbon disc, a platinum wire and a saturated calomel electrode

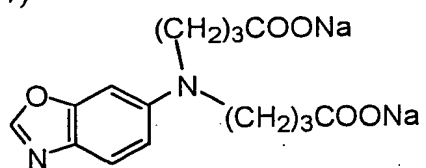
(SCE) are used as a working electrode, a counter electrode and a reference electrode, respectively. Measurement is performed at 25°C, at a potential scanning speed of 0.1 V/sec. At a time of a peak potential of a cyclic voltammetry wave, a ratio of an oxidation potential versus SCE is detected. E1 values of these compounds A-B are disclosed in EP No. 93,731A1.

Measurement of oxidation potential of radicals is performed by excessive electrochemistry and pulse radiolysis. These are reported in J. Am. Chem. Soc., 1988, 110, 132; 1974, 96, 1287; and 1974, 96, 1295.

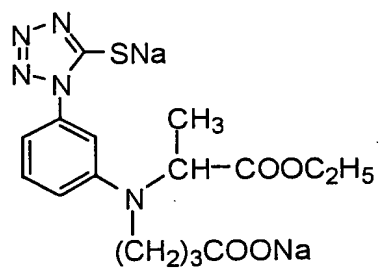
The following are specific examples of the compound represented by general formula (I), but the compounds to be used for the present invention are not restricted to them.



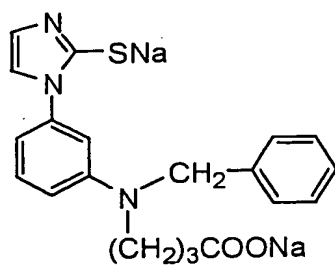
(I-7)



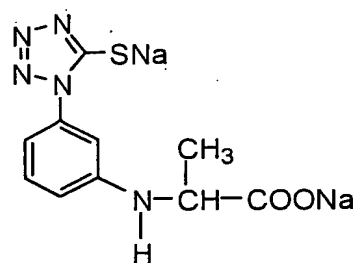
(I-8)



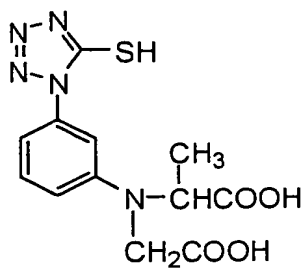
(I-9)



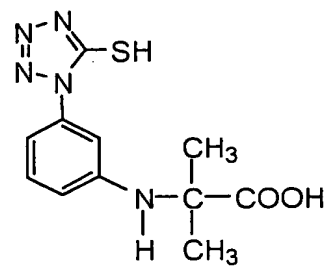
(I-10)

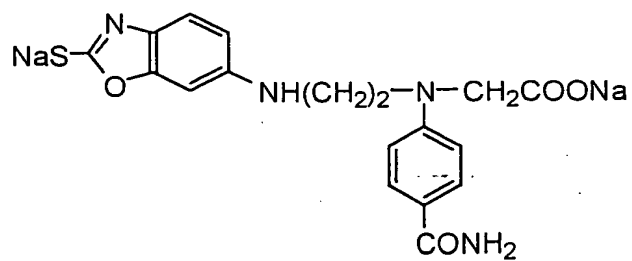
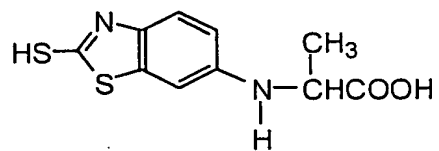
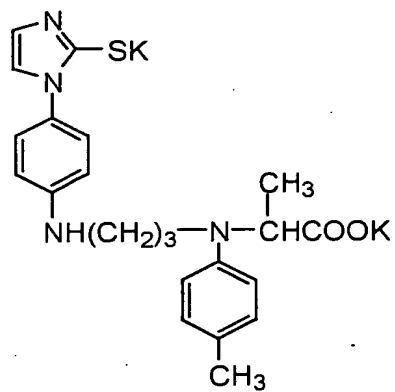
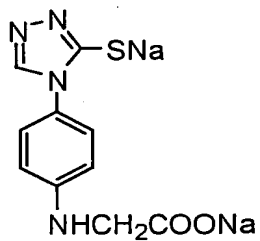
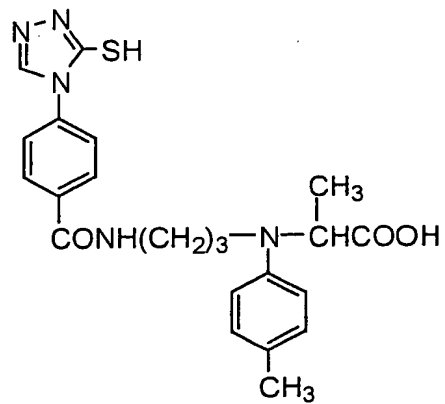
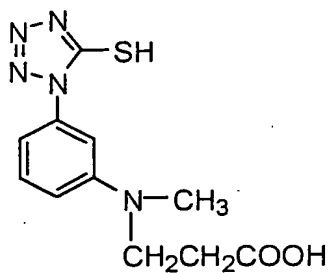


(I-11)



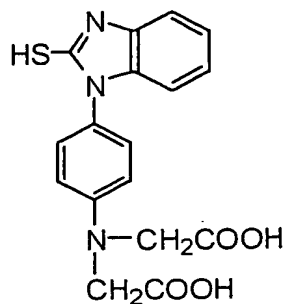
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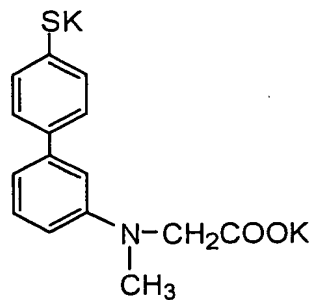




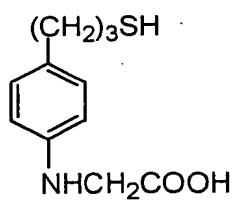
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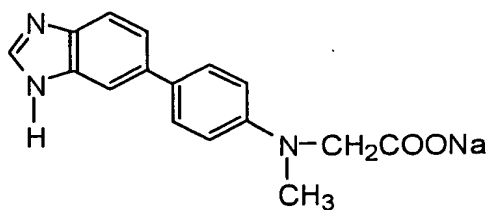
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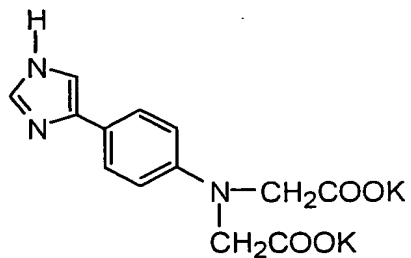
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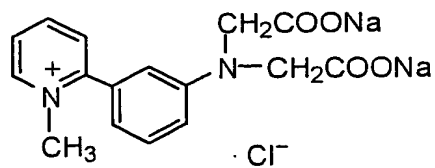
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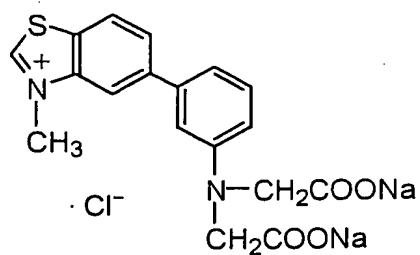
(I-23)



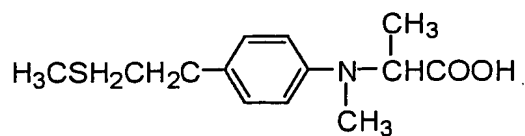
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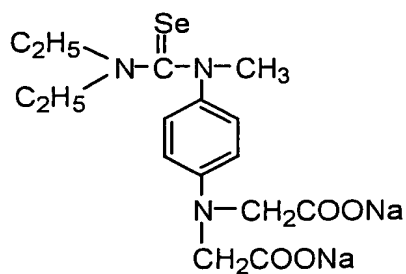
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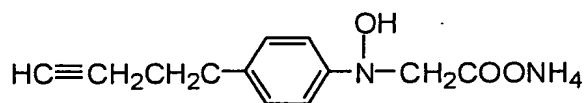
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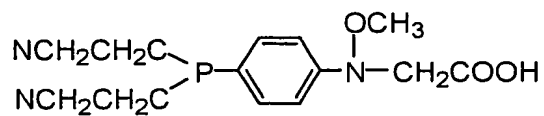
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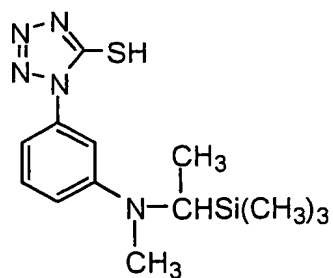
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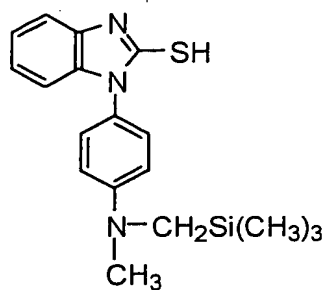
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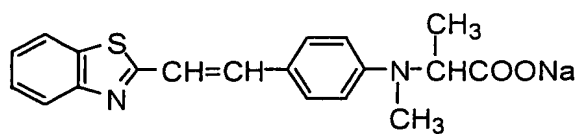
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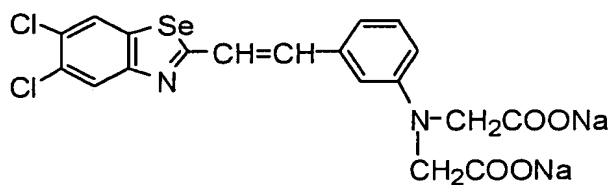
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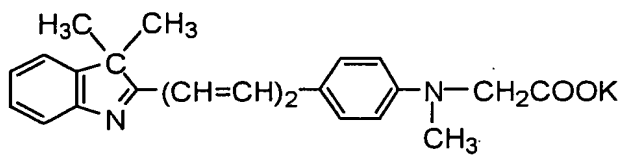
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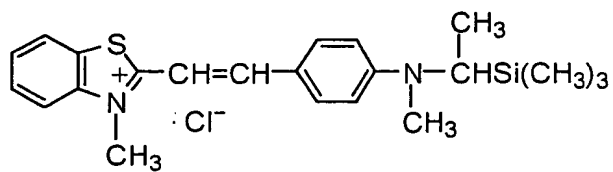
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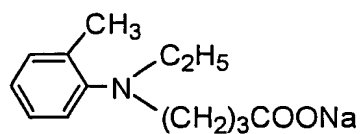
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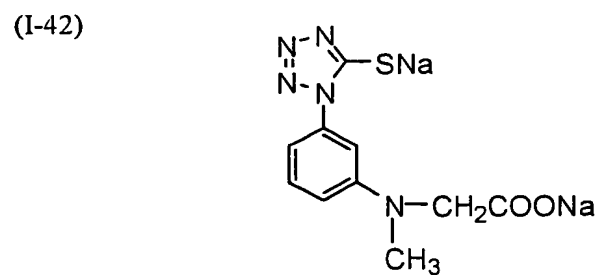
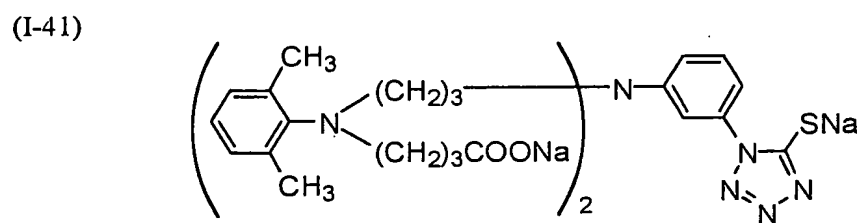
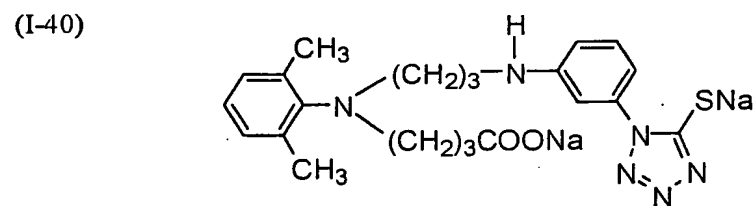
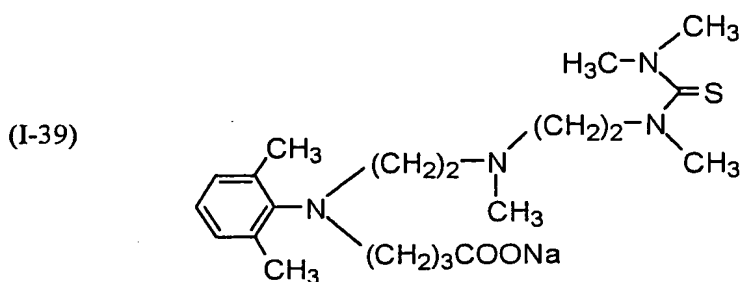
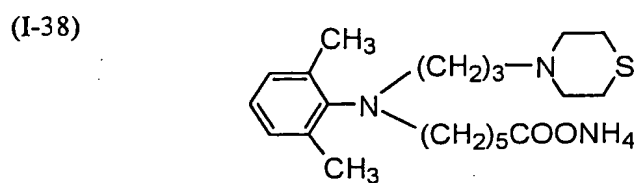
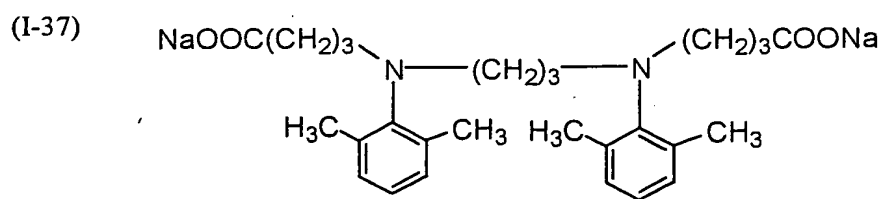


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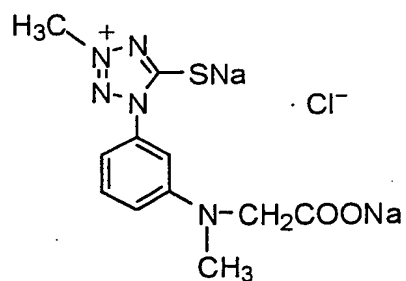


(I-36)

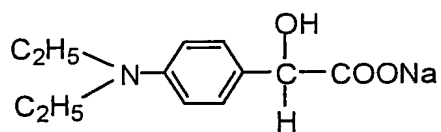




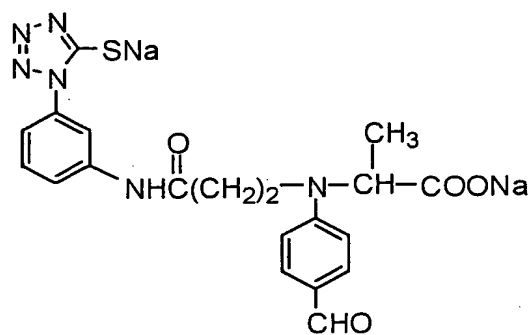
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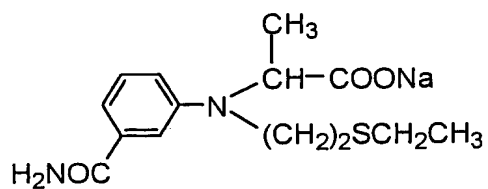
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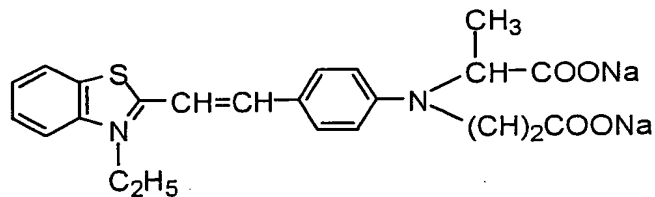
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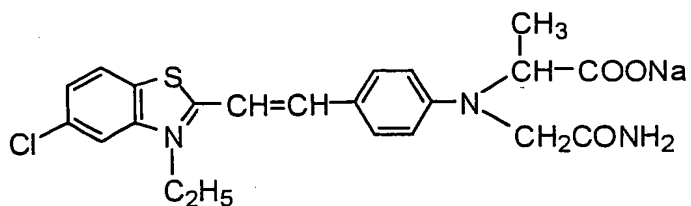
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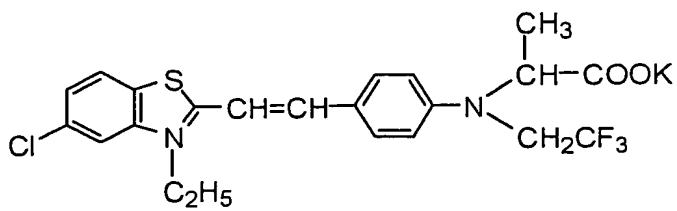
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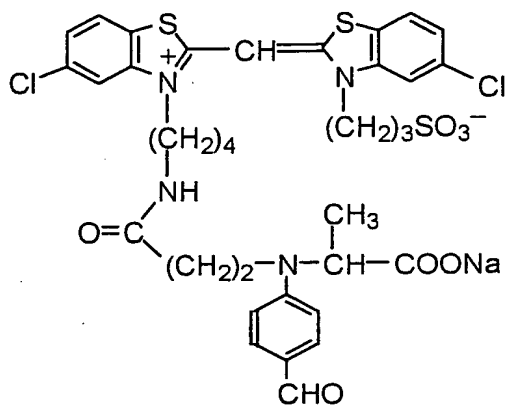
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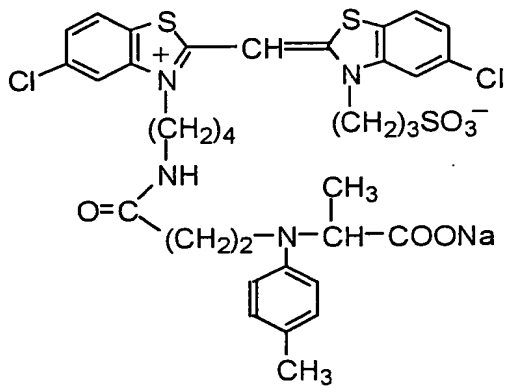
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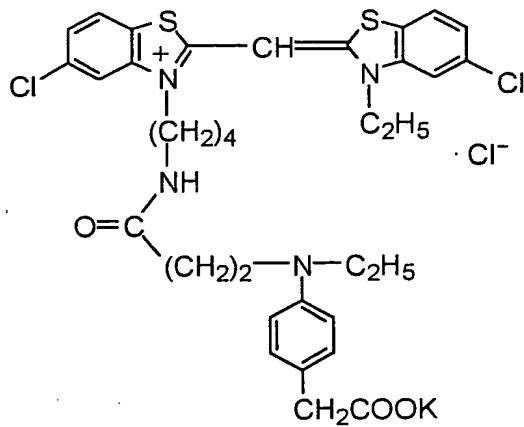
(I-50)



(I-51)



(1-52)



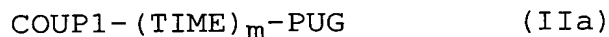
Next, a photographically useful group-releasing compound represented by general formula (II) will be described in detail:



5 wherein COUP1 represents a coupler residue that releases D1 by a coupling reaction with the oxidized form of a developing agent and also forms a water-soluble or alkali-soluble compound; and D1 represents a photographically useful group or its precursor that  
10 connects at the coupling position of COUP1.

The photographically useful group-releasing compound represented by general formula (II) will be described.

15 In detail, the photographically useful group-releasing compound represented by general formula (II) is represented by the following general formula (IIa) or (IIb).



20 In the formulas, COUP1 represents a coupler residue that releases (TIME)<sub>m</sub>-PUG or (TIME)<sub>i</sub>-RED-PUG by a coupling reaction with the oxidized form of a developing agent and also forms a water-soluble or alkali-soluble compound; TIME represents a timing group  
25 that cleave PUG or RED-PUG after its release from COUP1 by the coupling reaction; RED represents a group that reacts with the oxidized form of the developing agent

after its release, thereby cleaving PUG; PUG represents a photographically useful group; m represents an integer of 0 to 2; and i represents 0 or 1. When m is 2, the two TIMES are the same or different.

5           If COUP1 represents a yellow coupler residue, examples of this coupler residue are a pivaloylacetanilide type coupler residue, benzoylacetanilide type coupler residue, malondiesther type coupler residue, malondiamide type coupler residue,  
10           dibenzoylmethane type coupler residue, benzothiazolylacetamide type coupler residue, malonestermonoamide type coupler residue, benzoxazolylacetamide type coupler residue, benzoimidazolylacetamide type coupler residue,  
15           quinazoline-4-one-2-ylacetanilide type coupler residue, and cycloalkanoylacetylamine type coupler residue.

          If COUP1 represents a magenta coupler residue, examples of this coupler residue are a 5-pyrazolone type coupler residue, pyrazolo[1,5-a]benzimidazole type  
20           coupler residue, pyrazolo[1,5-b][1,2,4]triazole type coupler residue, pyrazolo[5,1-c][1,2,4]triazole type coupler residue, imidazo[1,2-b]pyrazole type coupler residue, pyrrolo[1,2-b][1,2,4]triazole type coupler residue, pyrazolo[1,5-b]pyrazole type coupler residue,  
25           and cyanoacetophenone type coupler residue.

          If COUP1 represents a cyan coupler residue, examples of this coupler residue are a phenol type

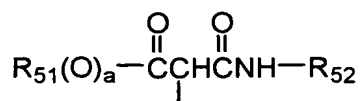


coupler residue, naphthol type coupler residue,  
pyrrolo[1,2-b][1,2,4]triazole type coupler residue,  
pyrrolo[2,1-c][1,2,4]triazole type coupler residue, and  
2,4-diphenylimidazole type coupler residue.

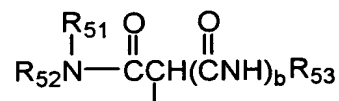
5 COUP1 can also be a coupler residue that does not  
substantially leave any color image. Examples of a  
coupler residue of this type are indanone type and  
acetophenone type coupler residues.

10 Preferable examples of COUP1 are coupler residues  
represented by formulas (Cp-1), (Cp-2), (Cp-3), (Cp-4),  
(Cp-5), (Cp-6), (Cp-7), (Cp-8), (Cp-9), (Cp-10), (Cp-  
11) and (Cp-12) below. These couplers are preferable  
because of their high coupling rates.

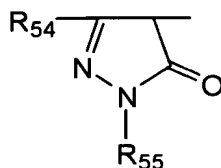
(Cp-1)



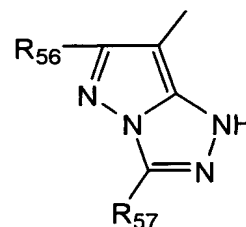
(Cp-2)



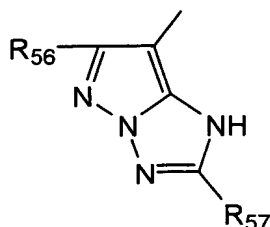
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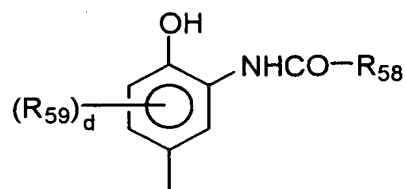
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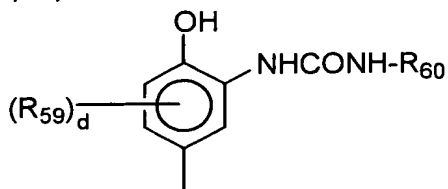
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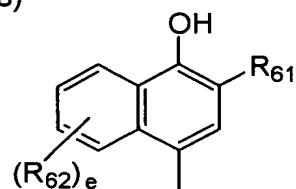
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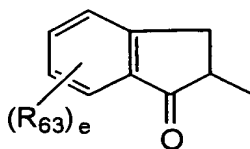
(Cp-7)



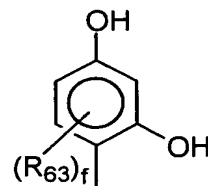
(Cp-8)



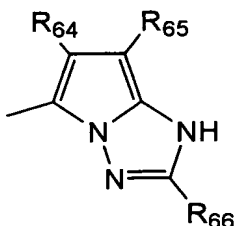
(Cp-9)



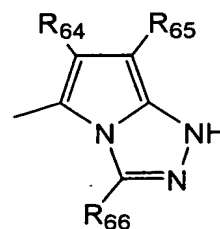
(Cp-10)



(Cp-11)



(Cp-12)



5 In the above formulas, a free bond hand stemming from the coupling position represents the bonding position of a coupling split-off group.

In the above formulas, the number of carbon atoms of each of R51, R52, R53, R54, R55, R56, R57, R58, R59, R60, R61, R62, R63, R64, R65 and R66 is preferably 10  
10 or less.

A coupler residue represented by COUP1 preferably has at least one substituent selected from an R71OCO-group, HOSO2- group, HO- group, R72NHCO- group and  
15 R72NHSO2- group. That is, at least one of R51 and R52 in formula (Cp-1), at least one of R51, R52 and R53 in formula (Cp-2), at least one of R54 and R55 in formula

(Cp-3), at least one of R<sub>56</sub> and R<sub>57</sub> in formulas (Cp-4) and (Cp-5), at least one of R<sub>58</sub> and R<sub>59</sub> in formula (Cp-6), at least one of R<sub>59</sub> and R<sub>60</sub> in formula (Cp-7), at least one of R<sub>61</sub> and R<sub>62</sub> in formula (Cp-8), at least one R<sub>63</sub> in formulas (Cp-9) and (Cp-10), and at least one of R<sub>64</sub>, R<sub>65</sub>, and R<sub>66</sub> in formulas (Cp-11) and (Cp-12) preferably have at least one substituent selected from an R<sub>71</sub>OCO- group, HOSO<sub>2</sub>- group, HO- group, R<sub>72</sub>NHCO- group, and R<sub>72</sub>NHSO<sub>2</sub>- group. R<sub>71</sub> represents a hydrogen atom, an alkyl group (e.g., methyl, ethyl, propyl, isopropyl, butyl and t-butyl) having 6 or less carbon atoms, or a phenyl group. R<sub>72</sub> represents a group represented by R<sub>71</sub>, R<sub>74</sub>CO- group, R<sub>74</sub>N(R<sub>75</sub>)CO- group, R<sub>73</sub>SO<sub>2</sub>- group or R<sub>74</sub>N(R<sub>75</sub>)SO<sub>2</sub>- group. R<sub>73</sub> represents an alkyl group (e.g., methyl, ethyl, propyl, isopropyl, butyl or t-butyl) having 6 or less carbon atoms, or a phenyl group. Each of R<sub>74</sub> and R<sub>75</sub> represents a group represented by R<sub>71</sub>. These groups can further have a substituent.

R<sub>51</sub> to R<sub>66</sub>, a, b, d, e, and f will be described in detail below. In the following description, R<sub>41</sub> represents an aliphatic hydrocarbon group, an aryl group or a heterocyclic group. R<sub>42</sub> represents an aryl group or a heterocyclic group. Each of R<sub>43</sub>, R<sub>44</sub> and R<sub>45</sub> represents a hydrogen atom, an aliphatic hydrocarbon group, an aryl group or a heterocyclic group.

R<sub>51</sub> represents the same meaning as R<sub>41</sub>. a represents 0 or 1. Each of R<sub>52</sub> and R<sub>53</sub> represents the same meaning as R<sub>43</sub>. If R<sub>52</sub> is not a hydrogen atom in formula (Cp-2), R<sub>52</sub> and R<sub>51</sub> can combine with each other to form a 5- to 7-membered ring. b represents 0 or 1.

R<sub>54</sub> represents a group having the same meaning as R<sub>41</sub>, R<sub>41</sub>CON(R<sub>43</sub>)- group, R<sub>41</sub>SO<sub>2</sub>N(R<sub>43</sub>)- group, R<sub>41</sub>N(R<sub>43</sub>)- group, R<sub>41</sub>S- group, R<sub>43</sub>O- group or R<sub>45</sub>N(R<sub>43</sub>)CON(R<sub>44</sub>)- group. R<sub>55</sub> represents a group having the same meaning as R<sub>41</sub>.

Each of R<sub>56</sub> and R<sub>57</sub> independently represents a group having the same meaning as R<sub>43</sub>, R<sub>41</sub>S- group, R<sub>43</sub>O- group, R<sub>41</sub>CON(R<sub>43</sub>)- group, R<sub>41</sub>OCN(R<sub>43</sub>)- group or R<sub>41</sub>SO<sub>2</sub>N(R<sub>43</sub>)- group.

R<sub>58</sub> represents a group having the same meaning as R<sub>43</sub>. R<sub>59</sub> represents a group having the same meaning as R<sub>41</sub>, R<sub>41</sub>CON(R<sub>43</sub>)- group, R<sub>41</sub>OCN(R<sub>43</sub>)- group, R<sub>41</sub>SO<sub>2</sub>N(R<sub>43</sub>)- group, R<sub>43</sub>N(R<sub>44</sub>)CON(R<sub>45</sub>)- group, R<sub>41</sub>O- group, R<sub>41</sub>S- group, a halogen atom or R<sub>41</sub>N(R<sub>43</sub>)- group. d represents 0 to 3. If d is the plural number, a plurality of R<sub>59</sub>'s represent the same substituent or different substituents.

R<sub>60</sub> represents a group having the same meaning as R<sub>43</sub>.

R<sub>61</sub> represents a group having the same meaning as R<sub>43</sub>, R<sub>43</sub>OSO<sub>2</sub>- group, R<sub>43</sub>N(R<sub>44</sub>)SO<sub>2</sub>- group, R<sub>43</sub>OCO- group, R<sub>43</sub>N(R<sub>44</sub>)CO- group, a cyano group, R<sub>41</sub>SO<sub>2</sub> N(R<sub>43</sub>)CO-

group,  $R_{43}CON(R_{44})CO-$  group,  $R_{43}N(R_{44})SO_2N(R_{45})CO-$  group,  $R_{43}N(R_{44})CON(R_{45})CO-$  group,  $R_{43}N(R_{44})SO_2N(R_{45})SO_2-$  group or  $R_{43}N(R_{44})CON(R_{45})SO_2-$  group.

5             $R_{62}$  represents a group having the same meaning as  $R_{41}$ ,  $R_{41}CONH-$  group,  $R_{41}OCONH-$  group,  $R_{41}SO_2NH-$  group,  $R_{43}N(R_{44})CONH-$  group,  $R_{43}N(R_{44})SO_2NH-$  group,  $R_{43}O-$  group,  $R_{41}S-$  group, a halogen atom or  $R_{41}N(R_{43})-$  group. In formula (Cp-8),  $e$  represents an integer from 0 to 4.  
10        If  $e$  is 2 or more, a plurality of  $R_{62}$ 's represent the same substituent or different substituents.

$R_{63}$  represents a group having the same meaning as  $R_{41}$ ,  $R_{43}CON(R_{44})-$  group,  $R_{43}N(R_{44})CO-$  group,  $R_{41}SO_2N(R_{43})-$  group,  $R_{41}N(R_{43})SO_2-$  group,  $R_{41}SO_2-$  group,  
15         $R_{43}OCO-$  group,  $R_{43}OSO_2-$  group, a halogen atom, a nitro group, a cyano group or  $R_{43}CO-$  group. In formula (Cp-9),  $e$  represents an integer from 0 to 4. If  $e$  is 2 or more, a plurality of  $R_{63}$ 's represent the same substituent or different substituents. In formula (Cp-  
20        10),  $f$  represents an integer from 0 to 3. If  $f$  is 2 or more, a plurality of  $R_{63}$ 's represent the same substituent or different substituents.

             Each of  $R_{64}$ ,  $R_{65}$  and  $R_{66}$  independently represents a group having the same meaning as  $R_{43}$ ,  $R_{41}S-$  group,  
25         $R_{43}O-$  group,  $R_{41}CON(R_{43})-$  group,  $R_{41}SO_2N(R_{43})-$  group,  $R_{41}OCO-$  group,  $R_{41}OSO_2-$  group,  $R_{41}SO_2-$  group,  $R_{41}N(R_{43})CO-$  group,  $R_{41}N(R_{43})SO_2-$  group, a nitro group

or a cyano group.

In the above description, an aliphatic hydrocarbon group represented by R<sub>41</sub>, R<sub>43</sub>, R<sub>44</sub> or R<sub>45</sub> is a saturated or unsaturated, chainlike or cyclic, straight chain or branched, substituted or unsubstituted aliphatic hydrocarbon group having 1-10 carbon atoms, preferably 1-6 carbon atoms. Representative examples of this aliphatic hydrocarbon group are methyl, cyclopropyl, isopropyl, n-butyl, t-butyl, i-butyl, t-amyl, n-hexyl, cyclohexyl, 2-ethylhexyl, n-octyl, 1,1,3,3-tetramethylbutyl, n-decyl and allyl.

An aryl group represented by R<sub>41</sub>, R<sub>42</sub>, R<sub>43</sub>, R<sub>44</sub> or R<sub>45</sub> is an aryl group having 6-10 carbon atoms, preferably substituted or unsubstituted phenyl or substituted or unsubstituted naphthyl.

A heterocyclic group represented by R<sub>41</sub>, R<sub>42</sub>, R<sub>43</sub>, R<sub>44</sub> or R<sub>45</sub> is a preferably 3- to 8-membered, substituted or unsubstituted heterocyclic group having 1-10 carbon atoms, preferably 1-6 carbon atoms which contains a hetero atom selected from a nitrogen atom, oxygen atom and sulfur atom. Representative examples of this heterocyclic group are 2-pyridyl, 2-benzoxazolyl, 2-imidazolyl, 2-benzimidazolyl, 1-indolyl, 1,3,4-thiadiazol-2-yl, 1,2,4-triazol-2-yl and 1-indolynyl.

If the aliphatic hydrocarbon group, aryl group and heterocyclic group described above have substituents,

representative examples of the substituents are a halogen atom,  $R_{43}O-$  group,  $R_{41}S-$  group,  $R_{43}CON(R_{44})-$  group,  $R_{43}N(R_{44})CO-$  group,  $R_{41}OCON(R_{43})-$  group,  $R_{41}SO_2N(R_{43})-$  group,  $R_{43}N(R_{44})SO_2-$  group,  $R_{41}SO_2-$  group, 5  $R_{43}OCO-$  group,  $R_{41}SO_2O-$  group, a group having the same meaning as  $R_{41}$ ,  $R_{43}N(R_{44})-$  group,  $R_{41}CO_2-$  group,  $R_{41}OSO_2-$  group, a cyano group, and a nitro group.

Preferable ranges of  $R_{51}$  to  $R_{66}$ , a, b, d, e, and f will be described below.

10  $R_{51}$  is preferably an aliphatic hydrocarbon group or an aryl group. a is most preferably 1. Each of  $R_{52}$  and  $R_{55}$  is preferably an aryl group. If b is 1,  $R_{53}$  is preferably an aryl group; if b is 0,  $R_{53}$  is preferably a heterocyclic group.  $R_{54}$  is preferably an  $R_{41}CON(R_{43})-$  group or  $R_{41}N(R_{43})-$  group. Each of  $R_{56}$  and  $R_{57}$  is 15 preferably an aliphatic hydrocarbon group, an aryl group,  $R_{41}O-$  group, or  $R_{41}S-$  group.  $R_{58}$  is preferably an aliphatic hydrocarbon group or an aryl group.

In formula (Cp-6),  $R_{59}$  is preferably a chlorine 20 atom, aliphatic hydrocarbon group or  $R_{41}CON(R_{43})-$  group, and d is preferably 1 or 2.  $R_{60}$  is preferably an aryl group. In formula (Cp-7),  $R_{59}$  is preferably an  $R_{41}CON(R_{43})-$  group, and d is preferably 1.

$R_{61}$  is preferably an  $R_{43}OSO_2-$  group,  $R_{43}N(R_{44})SO_2-$  25 group,  $R_{43}OCO-$  group,  $R_{43}N(R_{44})CO-$ , a cyano group,  $R_{41}SO_2N(R_{43})CO-$  group,  $R_{43}CON(R_{44})CO-$  group,  $R_{43}N(R_{44})SO_2N(R_{45})CO-$  group or  $R_{43}N(R_{44})CON(R_{45})CO-$

group. In formula (Cp-8), e is preferably 0 or 1. R<sub>62</sub> is preferably an R<sub>41</sub>CON(R<sub>43</sub>)- group, R<sub>41</sub>CON(R<sub>43</sub>)- group or R<sub>41</sub>SO<sub>2</sub>N(R<sub>43</sub>)- group, and the substitution position of any of these substituents is preferably the 5-position of a naphthol ring.

In formula (Cp-9), R<sub>63</sub> is preferably an R<sub>41</sub>CON(R<sub>43</sub>)- group, R<sub>41</sub>SO<sub>2</sub>N(R<sub>43</sub>)- group, R<sub>41</sub>N(R<sub>43</sub>)SO<sub>2</sub>- group, R<sub>41</sub>SO<sub>2</sub>- group, R<sub>41</sub>N(R<sub>43</sub>)CO- group, a nitro group or a cyano group. e is preferably 1 or 2.

In formula (Cp-10), R<sub>63</sub> is preferably an R<sub>43</sub>N(R<sub>44</sub>)CO- group, R<sub>43</sub>OCO- group or R<sub>43</sub>CO- group. f is preferably 1 or 2.

In formulas (Cp-11) and (Cp-12), each of R<sub>64</sub> and R<sub>65</sub> is preferably an R<sub>41</sub>OCO- group, R<sub>41</sub>OSO<sub>2</sub>- group, R<sub>41</sub>SO<sub>2</sub>- group, R<sub>44</sub>N(R<sub>43</sub>)CO- group, R<sub>44</sub>N(R<sub>43</sub>)SO<sub>2</sub>- group or a cyano group, and most preferably an R<sub>41</sub>OCO- group, R<sub>44</sub>N(R<sub>43</sub>)CO- group or a cyano group. R<sub>66</sub> is preferably a group having the same meaning as R<sub>41</sub>. The total number of carbon atoms, including those of the substituent(s) that attaches thereto, of each of R<sub>51</sub> to R<sub>66</sub> is preferably 18 or less, and more preferably, 10 or less.

A photographically useful group represented by PUG will be described below.

A photographically useful group represented by PUG can be any photographically useful group known to those skilled in the art.



Examples include development inhibitors, bleaching accelerators, development accelerators, dyes, bleaching inhibitors, couplers, developing agents, development auxiliaries, reducing agent, silver halide solvents, silver complex forming agents, fixers, image toner, stabilizers, film hardeners, tanning agents, fogging agents, ultraviolet absorbents, antifoggants, nucleating agents, chemical or spectral sensitizers, desensitizers, and brightening agents. However, PUG is not limited to these examples.

Preferable examples of PUG are development inhibitors (e.g., development inhibitors described in U.S.P. Nos. 3,227,554, 3,384,657, 3,615,506, 3,617,291, 3,733,201, and 5,200,306, and British Patent No. 1450479), bleaching accelerators (e.g., bleaching accelerators described in Research Disclosure 1973, Item No. 11449 and EP No. 193389, and those described in JP-A's-61-201247, 4-350848, 4-350849, and 4-350853), development auxiliaries (e.g., development auxiliaries described in U.S.P. No. 4,859,578 and JP-A-10-48787), development accelerators (e.g., development accelerators described in U.S.P. No. 4,390,618 and JP-A-2-56543), reducing agents (e.g., reducing agents described in JP-A's-63-109439 and 63-128342), and brightening agents (e.g., brightening agents described in U.S.P. Nos. 4,774,181 and 5,236,804). The pKa of conjugate acid of PUG is preferably 13 or less, and

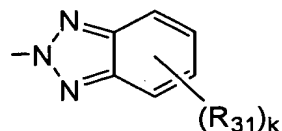
more preferably, 11 or less.

PUG is more preferably a development inhibitor or a bleaching accelerator.

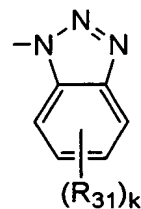
5        Preferable development inhibitors are a  
mercaptotetrazole derivative, a mercaptotriazole  
derivative, a mercaptothiadiazole derivative, a  
mercaptoxadiazole derivative, a mercaptoimidazole  
derivative, a mercaptobenzimidazole derivative, a  
mercaptobenzthiazole derivative, a mercaptobenzoxazole  
10       derivative, a tetrazole derivative, a 1,2,3-triazole  
derivative, a 1,2,4-triazole derivative and a  
benzotriazole derivative.

More preferable development inhibitors are represented by formulas DI-1 to DI-6 below.

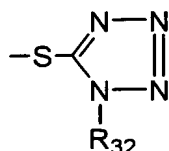
D I - 1



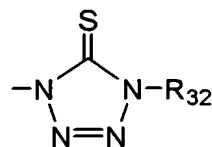
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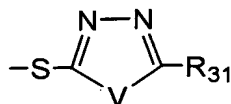
D I - 2



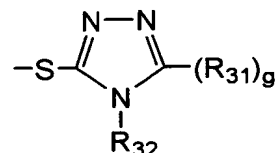
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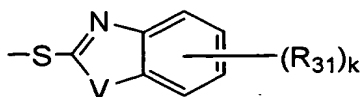
D I - 3



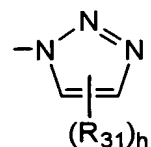
D I - 4



D I - 5



D I - 6



In the formula,  $R_{31}$  represents a halogen atom,  $R_{46}O-$  group,  $R_{46}S-$  group,  $R_{47}CON(R_{48})-$  group,  $R_{47}N(R_{48})CO-$  group,  $R_{46}OCON(R_{47})-$  group,  $R_{46}O_2(R_{47})-$  group,  $R_{47}N(R_{48})SO_2$  group,  $R_{46}SO_2-$  group,  $R_{47}OCO-$  group,  $R_{47}N(R_{48})CON(R_{49})-$  group,  $R_{47}CON(R_{48})SO_2-$  group,  $R_{47}N(R_{48})CON(R_{49})SO_2-$  group, group having the same meaning as  $R_{46}$ ,  $R_{47}N(R_{48})-$  group,  $R_{46}CO_2-$  group,  $R_{47}OSO_2-$  group, a cyano group or a nitro group.

$R_{46}$  represents an aliphatic hydrocarbon group, an aryl group or a heterocyclic group. Each of  $R_{47}$ ,  $R_{48}$  and  $R_{49}$  represents an aliphatic hydrocarbon group,

an aryl group, a heterocyclic group or a hydrogen atom.

An aliphatic hydrocarbon group represented by R<sub>46</sub>, R<sub>47</sub>, R<sub>48</sub> or R<sub>49</sub> is a saturated or unsaturated, chainlike or cyclic, straight chain or branched, substituted or

5 unsubstituted aliphatic hydrocarbon group having 1-32 carbon atoms, preferably 1-20 carbon atoms.

Representative examples are methyl, cyclopropyl, isopropyl, n-butyl, t-butyl, i-butyl, t-amyl, n-hexyl, cyclohexyl, 2-ethylhexyl, n-octyl, 1,1,3,3-  
10 tetramethylbutyl, n-decyl, allyl and ethynyl.

An aryl group represented by R<sub>46</sub>, R<sub>47</sub>, R<sub>48</sub> or R<sub>49</sub> is an aryl group having 6-32 carbon atoms, preferably a substituted or unsubstituted phenyl or a substituted or unsubstituted naphthyl.

15 A heterocyclic group represented by R<sub>46</sub>, R<sub>47</sub>, R<sub>48</sub> or R<sub>49</sub> is a preferably 3- to 8-membered, substituted or unsubstituted heterocyclic group having 1-32 carbon atoms, preferably 1-20 carbon atoms which contains a hetero atom selected from a nitrogen atom, an oxygen atom and a sulfur atom. Representative examples of  
20 this heterocyclic group are 2-pyridyl, 2-benzoxazolyl, 2-imidazolyl, 2-benzimidazolyl, 1-indolyl, 1,3,4-thiodiazol-2-yl, 1,2,4-triazol-2-yl or 1-indolinyl.

R<sub>32</sub> represents a group having the same meaning as  
25 R<sub>46</sub>.

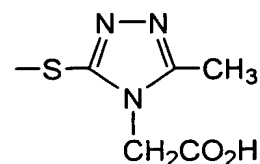
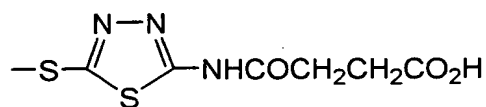
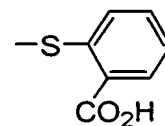
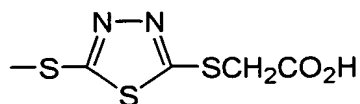
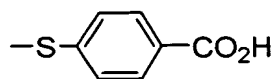
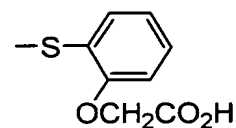
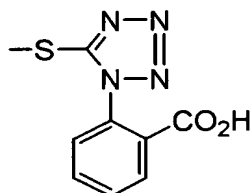
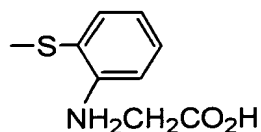
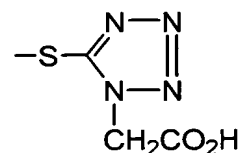
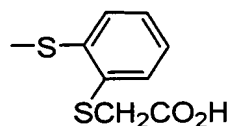
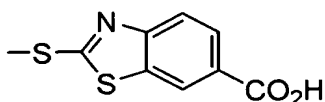
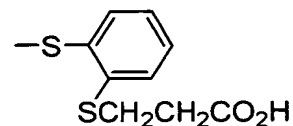
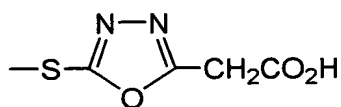
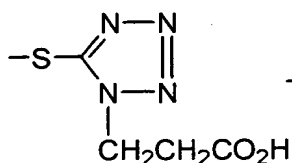
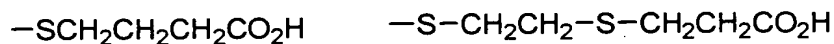
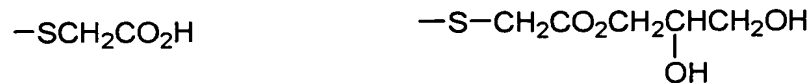
k represents an integer from 1 to 4, g represents 0 or 1, and h represents 1 or 2.

V represents an oxygen atom, a sulfur atom or -  
N(R<sub>46</sub>)-.

R<sub>31</sub> and R<sub>32</sub> may further have a substituent.

Preferable bleaching accelerators are as follows.

5



(Each free bonding hand bonds to the side of COUP1)

A group represented by TIME will be described next.

A group represented by TIME can be any linking

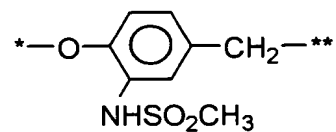
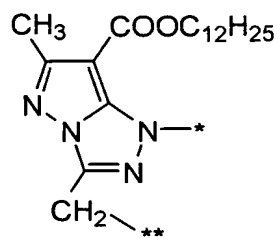
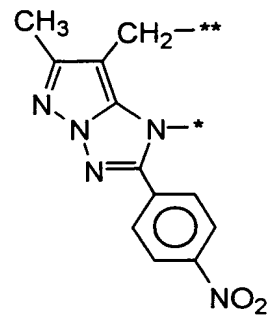
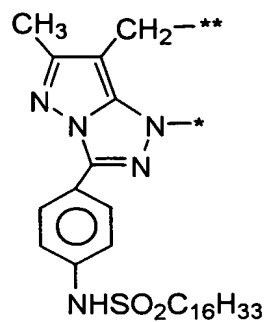
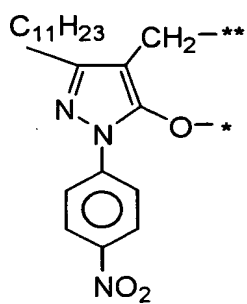
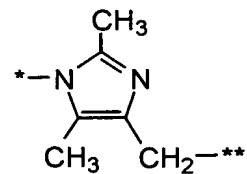
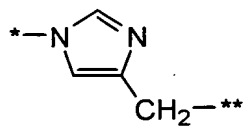
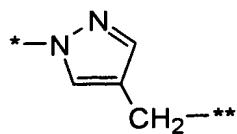
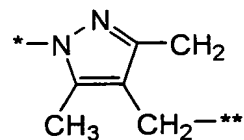
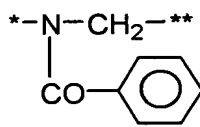
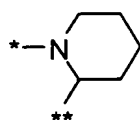
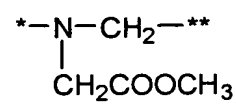
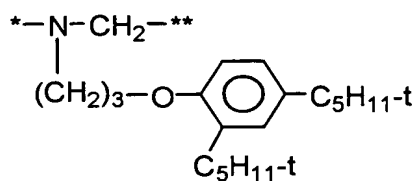
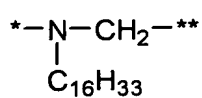
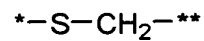
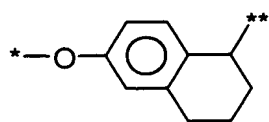
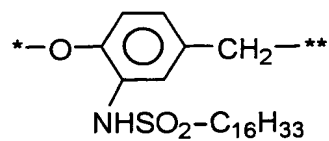
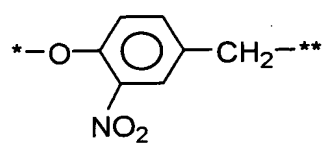
group which can cleave PUG or RED-PUG after being  
cleaved from COUP1 during development. Examples are a  
group described in U.S.P. Nos. 4,146,396, 4,652,516, or  
4,698,297, which uses a cleavage reaction of  
5 hemiacetal; a timing group described in U.S.P. Nos.  
4,248,962, 4,847,185 or 4,857,440, which causes a  
cleavage reaction by using an intramolecular  
nucleophilic substitution reaction; a timing group  
described in U.S.P. Nos. 4,409,323 or 4,421,845, which  
10 causes a cleavage reaction by using an electron  
transfer reaction; a group described in U.S.P. No.  
4,546,073, which causes a cleavage reaction by using a  
hydrolytic reaction of iminoketal; and a group  
described in West German Patent 2626317, which causes a  
15 cleavage reaction by using a hydrolytic reaction of  
ester. At a hetero atom, preferably an oxygen atom, a  
sulfur atom or a nitrogen atom contained in it, TIME  
bonds to COUP1 in general formula (IIa) or (IIb).  
Preferable examples of TIME are general formulas (T-1),  
20 (T-2) or (T-3) below.

General formula (T-1)	*-W-(X=Y) <sub>j</sub> -C(R <sub>21</sub> )R <sub>22</sub> -**
General formula (T-2)	*-W-CO-**
General formula (T-3)	*-W-LINK-E1-**

In the formulas, \* represents a position where  
25 TIME bonds to COUP1 in general formula (IIa) or (IIb),  
\*\* represents a position where TIME bonds to PUG,  
another TIME (if m is the plural number) or RED (in the

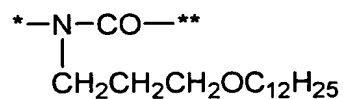
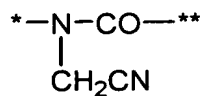
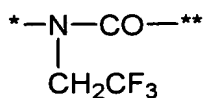
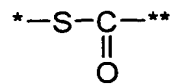
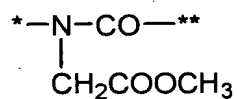
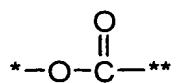
case of general formula (IIa)), W represents an oxygen atom, a sulfur atom or  $>N-R_{23}$ , each of X and Y represents methine or a nitrogen atom, j represents 0, 1, or 2, and each of  $R_{21}$ ,  $R_{22}$  and  $R_{23}$  represents a hydrogen atom or a substituent. If X and Y each represent substituted methine, this substituent and any two substituents of each of  $R_{21}$ ,  $R_{22}$  and  $R_{23}$  may connect to form a cyclic structure (e.g., a benzene ring or a pyrazole ring) or not. In general formula (T-3), E1 represents an electrophilic group. LINK represents a linking group which three-dimensionally relates W to E1 so as to allow an intramolecular nucleophilic substitution reaction.

Specific examples of TIME represented by general formula (T-1) are as follows.

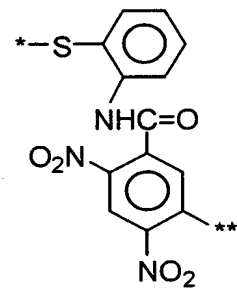
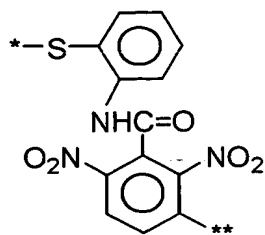
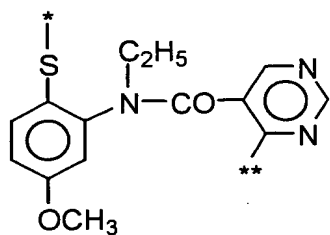
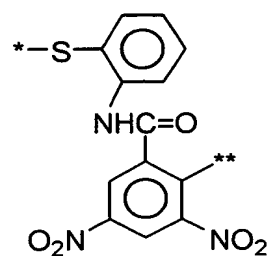
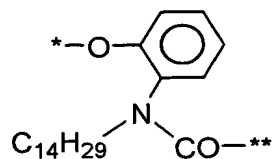
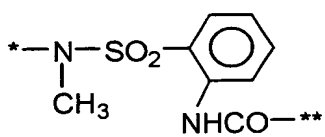
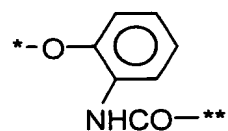
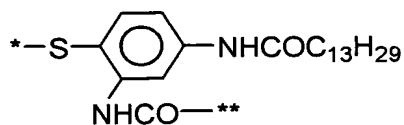
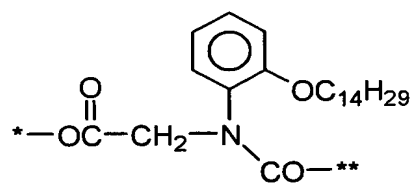
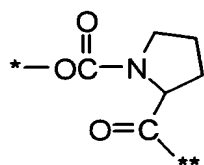
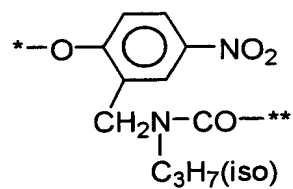
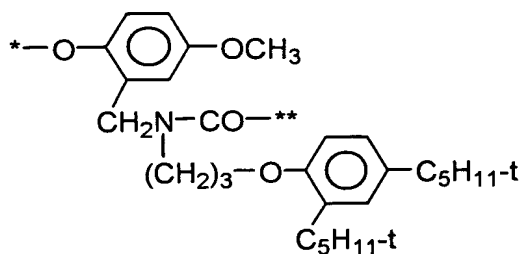
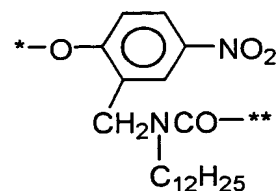
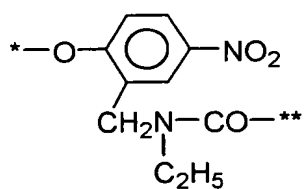




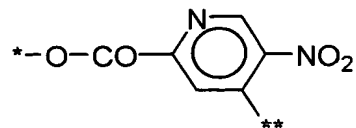
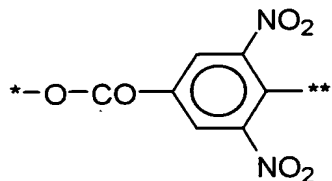
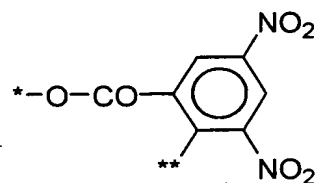
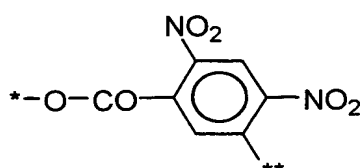
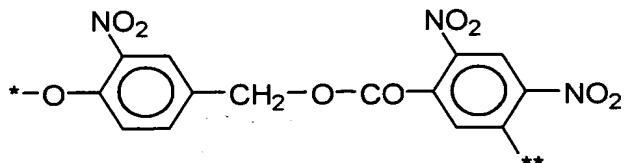
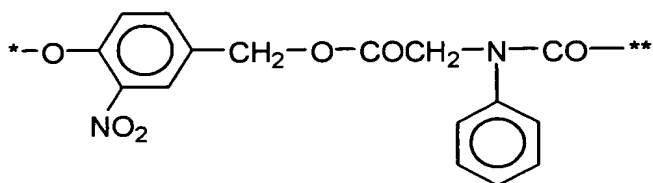
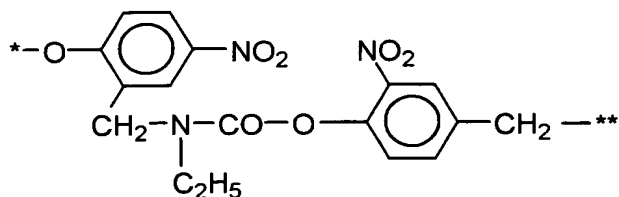
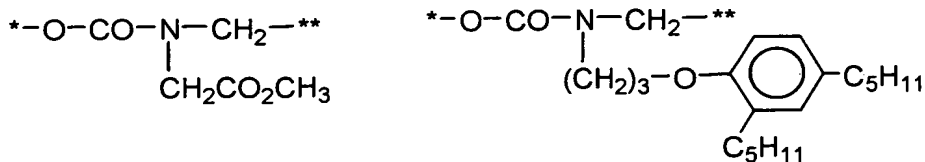
Specific examples of TIME represented by general formula (T-2) are as follows.



5 Specific examples of TIME represented by general formula (T-3) are as follows.



If m is 2 in general formula (IIa), specific examples of (TIME)<sub>m</sub> are as follows.



5

A group represented by RED in general formula (IIb) will be described below. RED is a group that cleaves from COUP1 or TIME to form RED-PUG and can be cross-oxidized by an acidic substance, such as the

oxidized form of a developing agent, present during development. RED-PUG can be any compound as long as it cleaves PUG when oxidized. Examples of RED are hydroquinones, catechols, pyrogallols, 1,4-naphthohydroquinones, 1,2-naphthohydroquinones, sulfonamidophenols, hydrazides and sulfonamidonaphthols. Specific examples of these groups will be described in JP-A's-61-230135, 62-251746 and 61-278852, U.S.P. Nos. 3,364,022, 3,379,529, 4,618,571, 3,639,417 and 4,684,604, and J. Org. Chem., Vol. 29, page 588 (1964).

Of these compounds, preferable examples of RED are hydroquinones, 1,4-naphthohydroquinones, 2-(or 4-)sulfonamidophenols, pyrogallols, and hydrazides. Of these compounds, a redox group having a phenolic hydroxyl group combines with COUPl or TIME at an oxygen atom of the phenol group.

In order for a compound represented by general formula (IIa) or (IIb) to be fixed to a lightsensitive layer or a non-lightsensitive layer to which the compound is added before a silver halide lightsensitive material containing the compound represented by general formula (IIa) or (IIb) is developed, a compound represented by general formula (IIa) or (IIb) preferably has a non-diffusing group. Most preferably, this non-diffusing group is contained in TIME or RED. Preferable examples of the non-diffusing group are an alkyl group having 8-40 carbon atoms, preferably 12-32

carbon atoms or an aryl group having 8-40 carbon atoms, preferably 12-32 carbon atoms that has at least one alkyl group (having 3-20 carbon atoms), an alkoxy group (having 3-20 carbon atoms) or an aryl group- (having 6-  
5 20 carbon atoms).

Methods of synthesizing compounds represented by general formulas (IIa) and (IIb) will be described in, e.g., the known patents and references cited to explain TIME, RED and PUG, JP-A's-61-156127, 58-160954, 58-  
10 162949, 61-249052 and 63-37350, U.S.P. No. 5,026,628, and EP Publication Nos. 443530A2 and 444501A2.

A photographically useful group-releasing compound represented by general formula (III) will be described below.

15 COUP2-C-E-D2 (III)

In the formula, COUP2 represents a coupler residue capable of coupling with the oxidized form of a developing agent, E represents an electrophilic portion, C represents a bivalent linking group or a single bond  
20 capable of releasing D2 with 4- to 8-membered ring formation by an intramolecular nucleophilic substitution reaction of a nitrogen atom, which arises from the developing agent in the product of coupling between COUP2 and the oxidized form of the developing  
25 agent and which directly bonds to the coupling position, with the nucleophilic portion E, which may bond to COUP2 either at a coupling position of COUP2 or at a

position of COUP2 other than its coupling position. D2 represents a photographically useful group or its precursor.

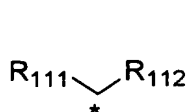
As a coupler residue represented by COUP2, coupler residues generally known as photographic couplers can be used. Examples are yellow coupler residues (e.g., open-chain ketomethine type coupler residues such as acylactanilide and malondianilide), magenta coupler residues (e.g., 5-pyrazolon type and pyrazolotriazole type coupler residues), and cyan coupler residues (e.g., phenol type, naphthol type, and pyrrolotriazole type coupler residues). It is also possible to use yellow, magenta, and cyan dye forming couplers having novel skeletons described in, e.g., U.S.P. No. 5,681,689, JP-A's-7-128824, 7-128823, 6-222526, 9-258400, 9-258401, 9-269573 and 6-27612. Other coupler residues can also be used (e.g., coupler residues described in U.S.P. Nos. 3,632,345 and 3,928,041, which form a colorless substance by reacting with the oxidized form of an aromatic amine-based developing agent and coupler residues described in U.S.P. Nos. 1,939,231 and 2,181,944, which form a black or intermediate-color substance by reacting with the oxidized form of an aromatic amine-based developing agent).

The coupler residue represented by COUP2 may be a monomer, and also may be dimer, oligomer or a part of a polymer coupler. In the latter case, the coupler may

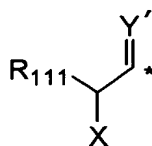
contain more than one PUG.

Preferable examples of COUP2 of the present invention will be presented below, but COUP2 is not limited to these examples.

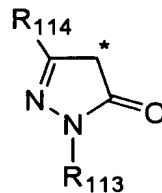
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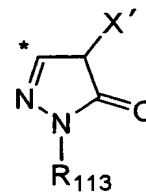
(III-1A)



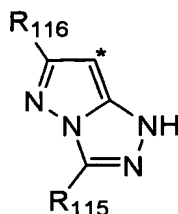
(III-2A)



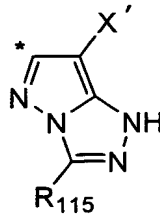
(III-1B)



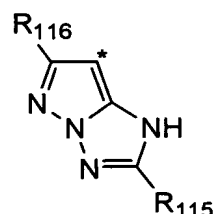
(III-2B)



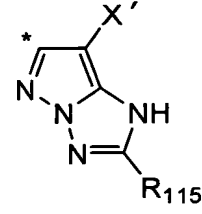
(III-1C)



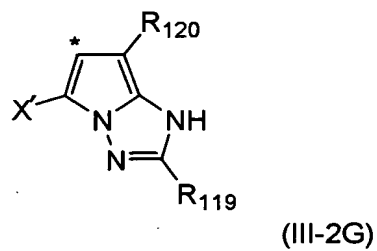
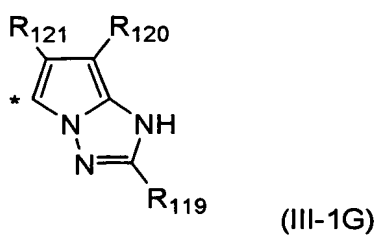
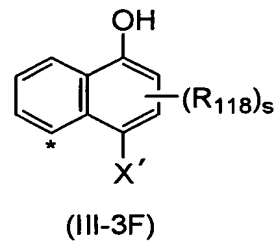
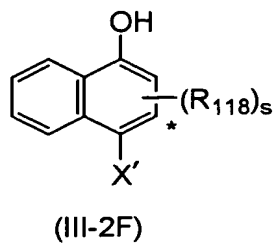
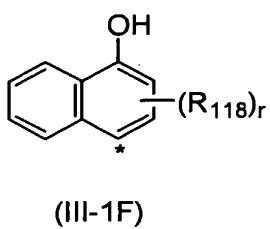
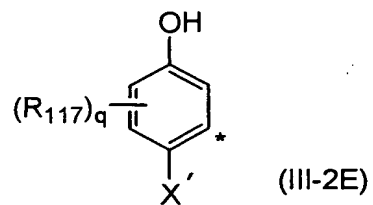
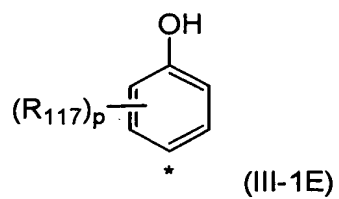
(III-2C)



(III-1D)



(III-2D)





wherein \* represents a position of bonding to C,  
X' represents a hydrogen atom, halogen atom (e.g.,  
a fluorine atom, chlorine atom, bromine atom, or  
iodine atom), R<sub>131</sub>-, R<sub>131</sub>O-, R<sub>131</sub>S-, R<sub>131</sub>OCOO-,  
5 R<sub>132</sub>COO-, R<sub>132</sub>(R<sub>133</sub>)NCOO-, or R<sub>132</sub>CON(R<sub>133</sub>)-, Y'  
represents an oxygen atom, sulfur atom, R<sub>132</sub>N=, or  
R<sub>132</sub>ON=.

R<sub>131</sub> represents an aliphatic group (an "aliphatic  
group" means a saturated or unsaturated, chain or  
10 cyclic, straight-chain or branched, and substituted or  
unsubstituted aliphatic hydrocarbon group, and an  
aliphatic group used in the following description has  
the same meaning), aryl group, or heterocyclic group.

The aliphatic group represented by R<sub>131</sub> is an  
15 aliphatic group having preferably 1 to 32 carbon atoms,  
and more preferably 1 to 22 carbon atoms. Examples are  
methyl, ethyl, vinyl, ethynyl, propyl, isopropyl,  
2-propenyl, 2-propynyl, butyl, isobutyl, t-butyl,  
t-amyl, hexyl, cyclohexyl, 2-ethylhexyl, octyl,  
20 1,1,3,3-tetramethylbutyl, decyl, dodecyl, hexadecyl,  
and octadecyl. If the aliphatic group is a substituted  
aliphatic group, the number of "carbon atoms" is the  
total number of carbon atoms including carbon atoms of  
the substituent. The number of carbon atoms of a group  
25 other than an aliphatic group also means the total  
number of carbon atoms including carbon atoms of  
a substituent.

The aryl group represented by  $R_{131}$  is a substituted or unsubstituted aryl group having preferably 6 to 32 carbon atoms, and more preferably 6 to 22 carbon atoms. Examples are phenyl, tolyl, and naphthyl.

The heterocyclic group represented by  $R_{131}$  is a substituted or unsubstituted heterocyclic group having preferably 1 to 32 carbon atoms, and more preferably 1 to 22 carbon atoms. Examples are 2-furyl, 2-pyrrolyl, 2-thienyl, 3-tetrahydrofuranyl 4-pyridyl, 2-pyrimidinyl, 2-(1,3,4-thiadiazolyl), 2-benzothiazolyl, 2-benzoxazolyl, 2-benzoimidazolyl, 2-benzoselenazolyl, 2-quinolyl, 2-oxazolyl, 2-thiazolyl, 2-selenazolyl, 5-tetrazolyl, 2-(1,3,4-oxadiazolyl), and 2-imidazolyl.

Each of  $R_{132}$  and  $R_{133}$  independently represents a hydrogen atom, aliphatic group, aryl group, or heterocyclic group. The aliphatic group, aryl group, and heterocyclic group represented by  $R_{132}$  and  $R_{133}$  have the same meanings as those represented by  $R_{131}$ , respectively.

Preferably,  $X'$  represents a hydrogen atom, aliphatic group, aliphatic oxy group, aliphatic thio group, or  $R_{132}CON(R_{133})-$ , and  $Y'$  represents an oxygen atom.

Examples of substituents suited to the groups described above and groups to be described below and examples of "substituents" to be described below are

a halogen atom (e.g., a fluorine atom, chlorine atom, bromine atom, and iodine atom), hydroxyl group, carboxyl group, sulfo group, cyano group, nitro group, alkyl group (e.g., methyl, ethyl, and hexyl),

5 fluoroalkyl group (e.g., trifluoromethyl), aryl group (e.g., phenyl, tolyl, and naphthyl), heterocyclic group (e.g., a heterocyclic group having the same meaning as R<sub>131</sub>), alkoxy group (e.g., methoxy, ethoxy, and octyloxy), aryloxy group (e.g., phenoxy and

10 naphthyloxy), alkylthio group (e.g., methylthio and butylthio), arylthio group (e.g., phenylthio), amino group (e.g., amino, N-methylamino, N,N-dimethylamino, and N-phenylamino), acyl group (e.g., acetyl, propionyl, and benzoyl), alkylsulfonyl and arylsulfonyl groups

15 (e.g., methylsulfonyl and phenylsulfonyl), acylamino group (e.g., acetylamino and benzoylamino), alkylsulfonylamino and arylsulfonylamino groups (e.g., methanesulfonylamino and benzenesulfonylamino), carbamoyl group (e.g., carbamoyl, N-methylaminocarbonyl, N,N-dimethylaminocarbonyl, and N-phenylaminocarbonyl),

20 sulfamoyl group (e.g., sulfamoyl, N-methylaminosulfonyl, N,N-dimethylaminosulfonyl, and N-phenylaminosulfonyl), alkoxycarbonyl group (e.g., methoxycarbonyl, ethoxycarbonyl, and octyloxycarbonyl), aryloxycarbonyl

25 group (e.g., phenoxycarbonyl and naphthyloxycarbonyl), acyloxy group (e.g., acetyloxy and benzoyloxy), alkoxycarbonyloxy group (e.g., methoxycarbonyloxy and

ethoxycarbonyloxy), aryloxy carbonyloxy group (e.g.,  
phenoxycarbonyloxy), alkoxycarbonylamino group (e.g.,  
methoxycarbonylamino and butoxycarbonylamino),  
aryloxy carbonylamino group (e.g., phenoxycarbonylamino),  
5 aminocarbonyloxy group (e.g., N-methylaminocarbonyloxy  
and N-phenylaminocarbonyloxy), aminocarbonylamino  
group (e.g., N-methylaminocarbonylamino and  
N-phenylaminocarbonylamino).

Each of  $R_{111}$  and  $R_{112}$  independently represents  
10  $R_{132}CO-$ ,  $R_{131}OCO-$ ,  $R_{132}(R_{133})NCO-$ ,  $R_{131}SO_n-$ ,  
 $R_{132}(R_{133})NSO_2-$ , or a cyano group.  $R_{131}$ ,  $R_{132}$ , and  
 $R_{133}$  have the same meanings as above.  $n$  represents 1  
or 2.

$R_{113}$  represents a group having the same meaning  
15 as  $R_{131}$ .

$R_{114}$  represents  $R_{132}-$ ,  $R_{132}CON(R_{133})-$ ,  
 $R_{132}(R_{133})N-$ ,  $R_{131}SO_2N(R_{132})-$ ,  $R_{131}S-$ ,  $R_{131}O-$ ,  
 $R_{131}OCON(R_{132})-$ ,  $R_{132}(R_{133})NCON(R_{134})-$ ,  $R_{131}OCO-$ ,  
 $R_{132}(R_{133})NCO-$ , or a cyano group.  $R_{131}$ ,  $R_{132}$ , and  $R_{133}$   
20 have the same meanings as above.  $R_{134}$  represents a  
group having the same meaning as  $R_{132}$ .

Each of  $R_{115}$  and  $R_{116}$  independently represents  
a substituent, preferably  $R_{132}-$ ,  $R_{132}CON(R_{133})-$ ,  
 $R_{131}SO_2N(R_{132})-$ ,  $R_{131}S-$ ,  $R_{131}O-$ ,  $R_{131}OCON(R_{132})-$ ,  
25  $R_{132}(R_{133})NCON(R_{134})-$ ,  $R_{131}OCO-$ ,  $R_{132}(R_{133})NCO-$ , a  
halogen atom, or cyano group, and more preferably a  
group represented by  $R_{131}$ .  $R_{131}$ ,  $R_{132}$ ,  $R_{133}$ , and  $R_{134}$

have the same meanings as above.

R<sub>117</sub> represents a substituent, p represents an integer from 0 to 4, and q represents an integer from 0 to 3. Preferable examples of a substituent represented  
5 by R<sub>117</sub> are R<sub>131</sub>-, R<sub>132</sub>CON(R<sub>133</sub>)-, R<sub>131</sub>OCON(R<sub>132</sub>)-,  
R<sub>131</sub>SO<sub>2</sub>N(R<sub>132</sub>)-, R<sub>132</sub>(R<sub>133</sub>)NCON(R<sub>134</sub>)-, R<sub>131</sub>S-, R<sub>131</sub>O-,  
and a halogen atom. R<sub>131</sub>, R<sub>132</sub>, R<sub>133</sub>, and R<sub>134</sub> have  
the same meanings as above. If p and q are 2 or more,  
a plurality of R<sub>117</sub>'s can be the same or different, and  
10 adjacent R<sub>117</sub>'s can combine with each other to form  
a ring. In preferable forms of formulas (III-1E) and  
(III-2E), at least one of the two ortho positions  
with respect to the hydroxyl group is substituted by  
R<sub>132</sub>CONH-, R<sub>131</sub>OCONH-, or R<sub>132</sub>(R<sub>133</sub>)NCONH-.

15 R<sub>118</sub> represents a substituent, r presents an  
integer from 0 to 6, and s represents an integer from 0  
to 5. Preferable examples of a substituent represented  
by R<sub>118</sub> are R<sub>132</sub>CON(R<sub>133</sub>)-, R<sub>131</sub>OCON(R<sub>132</sub>)-,  
R<sub>131</sub>SO<sub>2</sub>N(R<sub>132</sub>)-, R<sub>132</sub>(R<sub>133</sub>)NCON(R<sub>134</sub>)-, R<sub>131</sub>S-, R<sub>131</sub>O-,  
20 R<sub>132</sub>(R<sub>133</sub>)NCO-, R<sub>132</sub>(R<sub>133</sub>)NSO<sub>2</sub>-, R<sub>131</sub>OCO-, a cyano  
group, and halogen atom. R<sub>131</sub>, R<sub>132</sub>, R<sub>133</sub>, and R<sub>134</sub>  
have the same meanings as above. When r and s are 2 or  
more, a plurality of R<sub>118</sub>'s can be the same or  
different, and adjacent R<sub>118</sub>'s can combine with each  
25 other to form a ring. In preferable forms of formulas  
(III-1F), (III-2F), and (III-3F), an ortho position to  
a hydroxyl group is substituted by R<sub>132</sub>CONH-,

$R_{132}HNCONH-$ ,  $R_{132}(R_{133})NSO_2-$ , or  $R_{132}NHCO-$ .

$R_{119}$  represents a substituent, preferably  $R_{132}-$ ,  
 $R_{132}CON(R_{133})-$ ,  $R_{131}SO_2N(R_{132})-$ ,  $R_{131}S-$ ,  $R_{131}O-$ ,  
 $R_{131}OCON(R_{132})-$ ,  $R_{132}(R_{133})NCON(R_{134})-$ ,  $R_{131}OCO-$ ,  
5  $R_{132}(R_{133})NSO_2-$ ,  $R_{132}(R_{133})NCO-$ , a halogen atom, or  
cyano group, and more preferably a group represented by  
 $R_{131}$ .  $R_{131}$ ,  $R_{132}$ ,  $R_{133}$ , and  $R_{134}$  have the same  
meanings as above.

Each of  $R_{120}$  and  $R_{121}$  independently represents  
10 a substituent, preferably  $R_{132}-$ ,  $R_{132}CON(R_{133})-$ ,  
 $R_{131}SO_2N(R_{132})-$ ,  $R_{131}S-$ ,  $R_{131}O-$ ,  $R_{131}OCON(R_{132})-$ ,  
 $R_{132}(R_{133})NCON(R_{134})-$ ,  $R_{132}(R_{133})NCO-$ ,  $R_{132}(R_{133})NSO_2-$ ,  
 $R_{131}OCO-$ , a halogen atom, or cyano group, and  
more preferably  $R_{132}(R_{133})NCO-$ ,  $R_{132}(R_{133})NSO_2-$ ,  
15 a trifluoromethyl group,  $R_{131}OCO-$ , or cyano group.  
 $R_{131}$ ,  $R_{132}$ ,  $R_{133}$ , and  $R_{134}$  have the same meanings as  
above.

$E$  represents an electrophilic group such as  $-CO-$ ,  
 $-CS-$ ,  $-COCO-$ ,  $-SO-$ ,  $-SO_2-$ ,  $-P(=O)(R_{151})-$ , or  
20  $-P(=S)(R_{151})-$ , wherein  $R_{151}$  represents an aliphatic  
group, aryl group, aliphatic oxy group, aryloxy group,  
aliphatic thio group, or arylthio group, and  
preferably  $-CO-$ .

$C$  represents a linking group or bivalent group  
25 capable of releasing  $D_2$ , along with formation of a  
ring, that is preferably a 4- to 8-membered ring, more  
preferably a 5- to 7-membered ring, and much more

preferably a 6-membered ring, by intramolecular nucleophilic substitution between the electrophilic portion E and the nitrogen atom, which arises from a developing agent and directly bonds to the coupling position in the coupling product obtained by the coupling of COUP2 with an oxidized form of a developing agent.

Examples of the connecting groups represented by C include:

- 10  $x-(CO)_{n1}-(Y')_{n2}-\{C(R_{141})(R_{142})\}_{n4}-xx,$   
 $x-(CO)_{n1}-\{N(R_{143})\}_{n3}-\{C(R_{141})(R_{142})\}_{n4}-xx,$   
 $x-(Y')_{n2}-(CO)_{n1}-\{C(R_{141})(R_{142})\}_{n4}-xx,$   
 $x-\{N(R_{143})\}_{n3}-(CO)_{n1}-\{C(R_{141})(R_{142})\}_{n4}-xx,$   
 $x-(CO)_{n1}-\{C(R_{141})(R_{142})\}_{n4}-(Y')_{n2}-xx,$   
15  $x-(CO)_{n1}-\{C(R_{141})(R_{142})\}_{n4}-\{N(R_{143})\}_{n3}-xx,$   
 $x-(Y')_{n2}-xx, \text{ and } x-\{N(R_{143})\}_{n3}-xx.$

In the above formulae, x represents a site at which the connecting group is bonded with COUP, and xx represents a site at which the connecting group is bonded with E. Y' represents an oxygen atom or a sulfur atom. Each of R<sub>141</sub>, R<sub>142</sub> and R<sub>143</sub> represents a hydrogen atom, an aliphatic group, an aryl group or a heterocyclic group (the aliphatic group, aryl group and heterocyclic group have the same meaning as described with respect to R<sub>131</sub>), provided that two of R<sub>141</sub>, R<sub>142</sub> and R<sub>143</sub> may be bonded with each other or each of R<sub>141</sub>, R<sub>142</sub> and R<sub>143</sub> may be bonded with COUP2, so as to form a

ring.

R<sub>141</sub> and R<sub>142</sub> are preferably a hydrogen atom or an aliphatic hydrocarbon group, more preferably a hydrogen atom.

5 R<sub>143</sub> is preferably a hydrogen atom or an aliphatic hydrocarbon group.

Each of n<sub>1</sub> and n<sub>3</sub> is an integer of 0 to 2, n<sub>2</sub> is 0 or 1, and n<sub>4</sub> is an integer of 1 to 5 (when n<sub>3</sub> and n<sub>4</sub> are an integer of 2 or more, relevant N(R<sub>143</sub>) moieties as well as C(R<sub>141</sub>)(R<sub>142</sub>) moieties may be identical with or different from each other). Further, n<sub>1</sub>+n<sub>2</sub>+n<sub>4</sub>, n<sub>1</sub>+n<sub>3</sub>+n<sub>4</sub>, n<sub>2</sub>, and n<sub>3</sub> are so selected that a 4 to 8-membered ring is formed through an intramolecular nucleophilic substitution reaction between the electrophilic moiety E and the nitrogen atom of a coupling product of COUP2 and a developing agent oxidation product, the nitrogen atom attributed to the developing agent and directly bonded to the coupling position. Provided, however, that when -N(R<sub>143</sub>)- is directly bonded with E, R<sub>143</sub> is not a hydrogen atom, and that when the connecting group C is connected to COUP2 at the coupling position thereof, the part directly connected to COUP2 is not -Y'-.

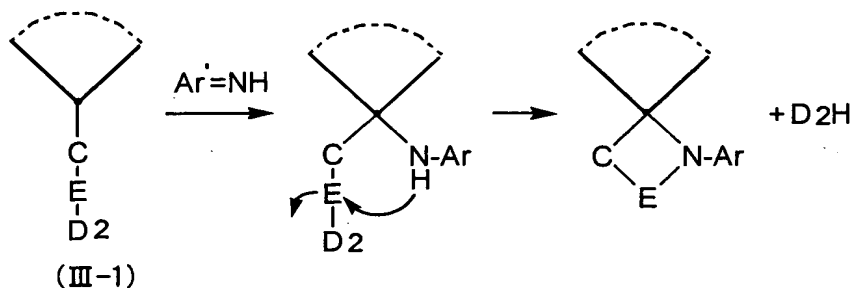
Although the position at which COUP2 is bonded with the connecting group C is not limited as long as D2 can be released while forming a (preferably 4 to 8-membered, more preferably 5 to 7-membered, and most



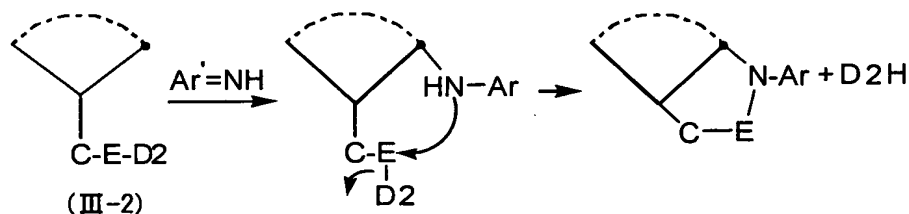
preferably 6-membered) ring through an intramolecular nucleophilic substitution reaction between the electrophilic moiety E and the nitrogen atom of a coupling product of COUP2 and a developing agent oxidation product, the nitrogen atom attributed to the developing agent, it is preferred that the position be the coupling position of COUP2 or position vicinal thereto, i.e., the atom adjacent to the coupling position or the atom adjacent to that adjacent atom.

When the connecting group C is bonded to the coupling position (1), or the atom adjacent to the coupling position (2), or the atom adjacent to the atom adjacent to the coupling position (3), of the coupler residue represented by COUP, the coupler of the present invention and the reaction between the coupler of the present invention and an oxidation product, i.e.,  $\text{Ar}' = \text{NH}$ , of an aromatic amine developing agent represented by the formula:  $\text{ArNH}_2$  can be expressed by the following formulae.

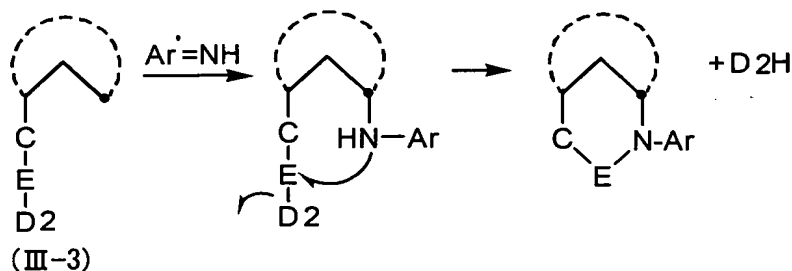
1) A case where C bonds at the coupling position of COUP2



2) A case where C bonds to an atom next to the coupling position of COUP2



3) A case where C bonds to an atom next to the next atom of the coupling position of COUP 2



and each represent a coupler residue capable of coupling with an oxidized form of a developing agent, which does not necessarily be a ring structure.

The mark "·" represents the coupling position.

The lines each represent a bonding between a non-metallic atom and a non-metallic atom.

Examples of the connecting groups C preferably used in the general formula (III-1) {wherein COUP2 is preferably represented by the formula (III-1A), (III-1B), (III-1C), (III-1D), (III-1E), (III-1F) or (IIII-1G)} include:

x-CO-C(R<sub>141</sub>)(R<sub>142</sub>)-C(R<sub>141</sub>)(R<sub>142</sub>)-xx,  
x-C(R<sub>141</sub>)(R<sub>142</sub>)-C(R<sub>141</sub>)(R<sub>142</sub>)-xx,  
x-C(R<sub>141</sub>)(R<sub>142</sub>)-C(R<sub>141</sub>)(R<sub>142</sub>)-C(R<sub>141</sub>)(R<sub>142</sub>)-xx,  
x-C(R<sub>141</sub>)(R<sub>142</sub>)-N(R<sub>143</sub>)-xx,  
x-C(R<sub>141</sub>)(R<sub>142</sub>)-C(R<sub>141</sub>)(R<sub>142</sub>)-O-xx,  
x-C(R<sub>141</sub>)(R<sub>142</sub>)-C(R<sub>141</sub>)(R<sub>142</sub>)-S-xx, and  
x-C(R<sub>141</sub>)(R<sub>142</sub>)-C(R<sub>141</sub>)(R<sub>142</sub>)-N(R<sub>143</sub>)-xx.

More preferred examples thereof are:

x-C(R<sub>141</sub>)(R<sub>142</sub>)-N(R<sub>143</sub>)-xx,  
x-C(R<sub>141</sub>)(R<sub>142</sub>)-C(R<sub>141</sub>)(R<sub>142</sub>)-O-xx, and  
x-C(R<sub>141</sub>)(R<sub>142</sub>)-C(R<sub>141</sub>)(R<sub>142</sub>)-N(R<sub>143</sub>)-xx.

In the above formulae, x, xx, R<sub>141</sub>, R<sub>142</sub> and R<sub>143</sub> are as defined above (when at least two -C(R<sub>141</sub>)(R<sub>142</sub>)- groups are present in one connecting group, relevant R<sub>141</sub> moieties as well as R<sub>142</sub> moieties may be identical with or different from each other).

Examples of the connecting groups C preferably used in the general formula (III-2) {wherein COUP2 is preferably represented by the formula (III-2A), (III-2B), (III-2C), (III-2D), (III-2E), (III-2F) or (III-2G)} include:

x-C(R<sub>141</sub>)(R<sub>142</sub>)-xx,

x-C(R<sub>141</sub>)(R<sub>142</sub>)-C(R<sub>141</sub>)(R<sub>142</sub>)-xx,  
x-O-xx, x-S-xx, x-N(R<sub>143</sub>)-xx,  
x-C(R<sub>141</sub>)(R<sub>142</sub>)-O-xx,  
x-C(R<sub>141</sub>)(R<sub>142</sub>)-S-xx, and  
5 x-C(R<sub>141</sub>)(R<sub>142</sub>)-N(R<sub>143</sub>)-xx.

More preferred examples thereof are:

x-O-xx, x-N(R<sub>143</sub>)-xx,  
x-C(R<sub>141</sub>)(R<sub>142</sub>)-O-xx, and  
x-C(R<sub>141</sub>)(R<sub>142</sub>)-N(R<sub>143</sub>)-xx.

10 In the above formulae, x, xx, R<sub>141</sub>, R<sub>142</sub> and R<sub>143</sub>  
are as defined above (when at least two -C(R<sub>141</sub>)(R<sub>142</sub>)-  
groups are present in one connecting group, relevant  
R<sub>141</sub> moieties as well as R<sub>142</sub> moieties may be identical  
with or different from each other).

15 Examples of the connecting groups C preferably  
used in the general formula (III-3) {wherein COUP2 is  
preferably represented by the formula (III-3F)} include  
x-C(R<sub>141</sub>)(R<sub>142</sub>)-xx, x-O-xx, x-S-xx, and x-N(R<sub>143</sub>)-xx.  
More preferred examples thereof are x-O-xx and  
20 x-N(R<sub>143</sub>)-xx. Most preferred examples thereof are  
x-N(R<sub>143</sub>)-xx. In the formulae, x, xx, R<sub>141</sub>, R<sub>142</sub> and  
R<sub>143</sub> are as defined above.

D2 represents a photographically useful group or  
its precursor. A preferable form of D2 is represented  
25 by formula (III-B) below



wherein # represents a portion coupling with E,

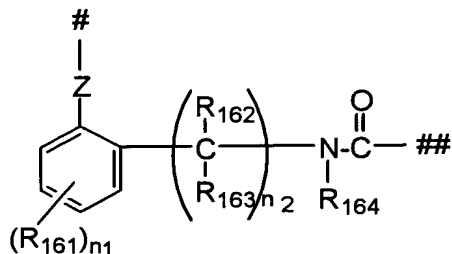
T represents a timing group capable of releasing PUG after being released from E, k represents an integer from 0 to 2, preferably 0 or 1, and PUG represents a photographically useful group.

5           Examples of a timing group represented by T are a group described in U.S.P. No. 4,146,396, 4,652,516, or 4,698,297, which releases PUG by using a cleavage reaction of hemiacetal; a group described in JP-A-9-114058 or U.S.P. No. 4,248,962, 5,719,017,  
10           or 5,709,987, which releases PUG by using an intramolecular ring closure reaction; a group described in JP-B-54-39727, JP-A-57-136640, JP-A-57-154234, JP-A-4-261530, JP-A-4-211246, JP-A-6-324439, JP-A-9-114058, or U.S.P. No. 4,409,323 or 4,421,845,  
15           which releases PUG by using electron transfer via  $\pi$  electrons; a group described in JP-A-57-179842, JP-A-4-261530, or JP-A-5-313322, which releases PUG by generating carbon dioxide; a group described in U.S.P. No. 4,546,073, which releases PUG by using a hydrolytic  
20           reaction of iminoketal; a group described in laid-open West German Patent 2,626,317, which releases PUG by using a hydrolytic reaction of ester; and a group described in EP572084, which releases PUG by using a reaction with sulfurous acid ions, the disclosures of  
25           all the references are herein incorporated by reference.

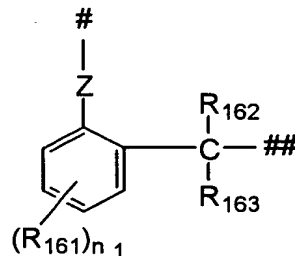
          Preferable examples of the timing group represented by T in formula (III) of the present

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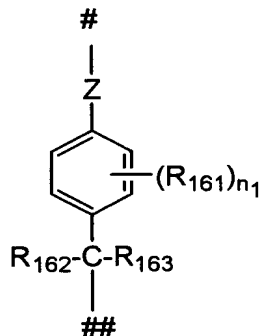
(T1)



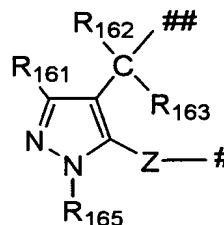
(T2)



(T3)



(T4)



5 wherein # represents a portion coupling with the electrophilic portion E or ##, and ## represents a position coupling with PUG or #. Z represents an oxygen atom or sulfur atom, preferably an oxygen atom. R<sub>161</sub> represents a substituent, preferably R<sub>131</sub>-,  
 10 R<sub>132</sub>CON(R<sub>133</sub>)-, R<sub>131</sub>SO<sub>2</sub>N(R<sub>132</sub>)-, R<sub>131</sub>S-, R<sub>131</sub>O-, R<sub>131</sub>OCON(R<sub>132</sub>)-, R<sub>132</sub>(R<sub>133</sub>)NCON(R<sub>134</sub>)-, R<sub>132</sub>(R<sub>133</sub>)NCO-, R<sub>132</sub>(R<sub>133</sub>)NSO<sub>2</sub>-, R<sub>131</sub>OCO-, a halogen atom, nitro group, or cyano group. R<sub>131</sub>, R<sub>132</sub>, R<sub>133</sub>, and R<sub>134</sub> have the same meanings as above. R<sub>161</sub> can combine with any of  
 15 R<sub>162</sub>, R<sub>163</sub>, and R<sub>164</sub> to form a ring. n<sub>1</sub> represents an integer from 0 to 4. When n<sub>1</sub> represents 2 or more, a plurality of R<sub>161</sub>'s can be the same or different and can combine with each other to form a ring.

Each of R<sub>162</sub>, R<sub>163</sub>, and R<sub>164</sub> independently represents a group having the same meaning as R<sub>132</sub>. n<sub>2</sub> represents 0 or 1. R<sub>162</sub> and R<sub>163</sub> can combine with each other to form a spiro ring. Each of R<sub>162</sub> and R<sub>163</sub> is preferably a hydrogen atom or an aliphatic group having 1 to 20, preferably 1 to 10 carbon atoms, and more preferably a hydrogen atom. R<sub>164</sub> is preferably an aliphatic group having 1 to 20, preferably 1 to 10 carbon atoms or an aryl group having 6 to 20, preferably 6 to 10 carbon atoms). R<sub>165</sub> represents R<sub>132</sub><sup>-</sup>, R<sub>132</sub>(R<sub>133</sub>)NCO<sup>-</sup>, R<sub>132</sub>(R<sub>133</sub>)NSO<sub>2</sub><sup>-</sup>, R<sub>131</sub>OCO<sup>-</sup>, or R<sub>132</sub>CO<sup>-</sup>. R<sub>131</sub>, R<sub>132</sub>, and R<sub>133</sub> have the same meanings as above. R<sub>165</sub> represents preferably R<sub>132</sub>, and more preferably an aryl group having 6 to 20 carbon atoms.

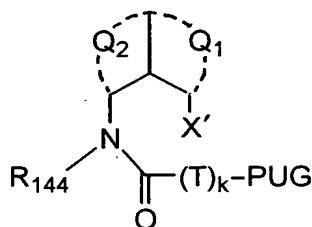
The photographically useful group represented by PUG has the same meaning as above.

In a preferred embodiment of the present invention, the coupler of the invention is represented by formula (III-2) or (III-3), and the coupler represented by formula (III-3) is more preferred, wherein C, E, and D<sub>2</sub>, and preferred A, E, and B are the same as those mentioned above.

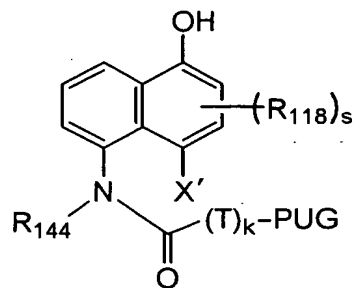
In a more preferred embodiment, the coupler represented by formula (III-3) is represented by formula (III-3a), the coupler represented by formula (III-3b) is much more preferred, and the coupler represented by formula (III-3c) is still much more



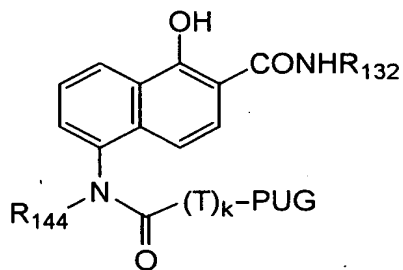
preferred. The structure of the cyclization product obtained by the reaction between the coupler represented by formula (III-3c) and the oxidized form, i.e.,  $\text{Ar}'=\text{NH}$ , of the aromatic amine developing agent, i.e.,  $\text{ArNH}_2$ , may be illustrate as follows:



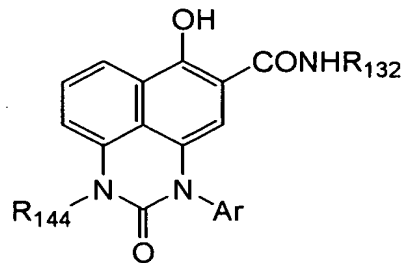
(III-3a)



(III-3b)



(III-3c)

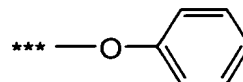
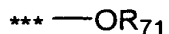


(III-C)

wherein  $Q_1$  and  $Q_2$  each represent a group of nonmetallic atoms required to form a 5-membered or 6-membered ring and induce the coupling reaction with a developing agent in a oxidized form at the atom of the joint part of  $X'$ ;  $X'$ ,  $T$ ,  $k$ ,  $\text{PUG}$ ,  $R_{118}$ ,  $s$ , and  $R_{132}$  are as defined above; and  $R_{144}$  represents a hydrogen atom, an aliphatic group, an aryl group, or a heterocyclic group, preferably an aliphatic group, an aryl group or a heterocyclic group, more preferably an aliphatic group.

The aliphatic group, aryl group and heterocyclic group are the same as defined above for R<sub>131</sub>.

In the present invention, D1 and D2 are not at least the following groups:



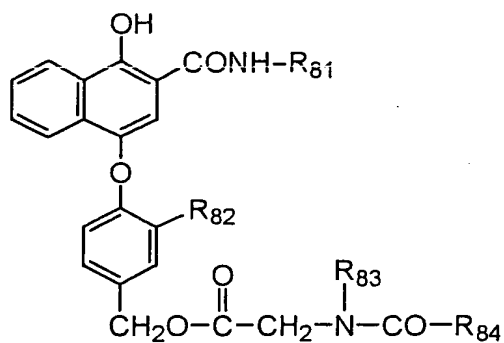
5

In the formulas, \*\*\* represents the portion at which it bonds to the electron attracting moiety represented by E or the timing group represented by T; R<sub>71</sub> represents a substituted or unsubstituted aliphatic hydrocarbon group; and R<sub>72</sub> represents an unsubstituted aliphatic hydrocarbon group.

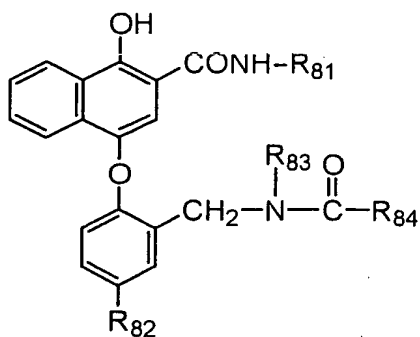
10

Examples of the couplers that may be used in the present invention are set forth below, but the present invention is not limited to these.

15

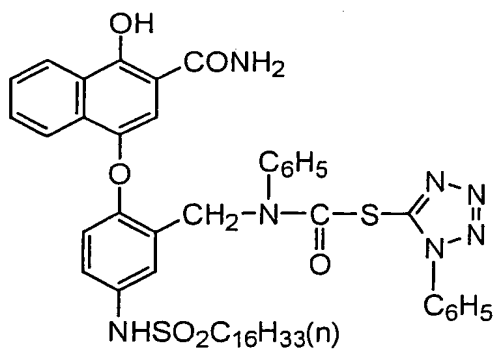


No.	R <sub>81</sub>	R <sub>82</sub>	R <sub>83</sub>	R <sub>84</sub>
II-1	-CH <sub>3</sub>	-NHSO <sub>2</sub> C <sub>16</sub> H <sub>33</sub> (n)	-C <sub>6</sub> H <sub>5</sub>	
II-2	-CH <sub>3</sub>	-NHSO <sub>2</sub> C <sub>16</sub> H <sub>33</sub> (n)	-C <sub>6</sub> H <sub>5</sub>	
II-3	-CH <sub>3</sub>	-NHSO <sub>2</sub> C <sub>16</sub> H <sub>33</sub> (n)	-C <sub>6</sub> H <sub>5</sub>	
II-4	-CH <sub>2</sub> CH <sub>2</sub> OCH <sub>3</sub>	-NHSO <sub>2</sub> C <sub>16</sub> H <sub>33</sub> (n)	-C <sub>6</sub> H <sub>5</sub>	-SCH <sub>2</sub> CH <sub>2</sub> CO <sub>2</sub> H
II-5		-NHSO <sub>2</sub> C <sub>16</sub> H <sub>33</sub> (n)	-C <sub>6</sub> H <sub>5</sub>	
II-6	-CH <sub>3</sub>	-NHSO <sub>2</sub> C <sub>16</sub> H <sub>33</sub> (n)		

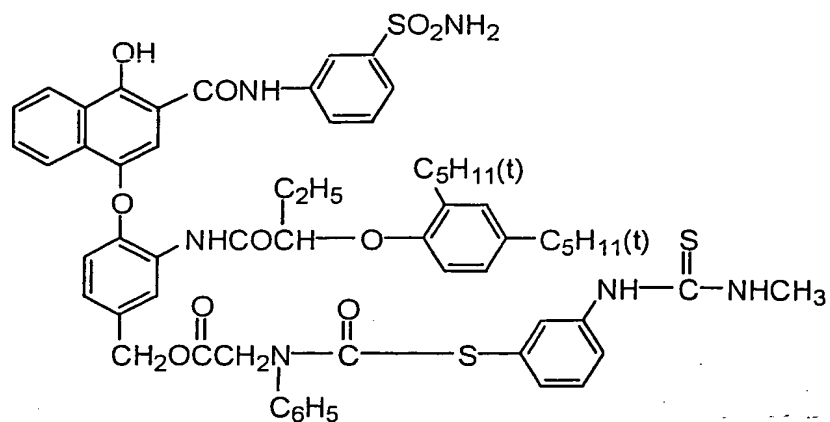


No.	R <sub>81</sub>	R <sub>82</sub>	R <sub>83</sub>	R <sub>84</sub>
II-7	$-(CH_2)_2CO_2C_2H_5$	$-NO_2$	$-C_{12}H_{25}(n)$	
II-8	$CH_3$	$-NO_2$	$-C_{12}H_{25}(n)$	
II-9	H	$-NHSO_2C_{16}H_{33}(n)$	$-C_6H_5$	

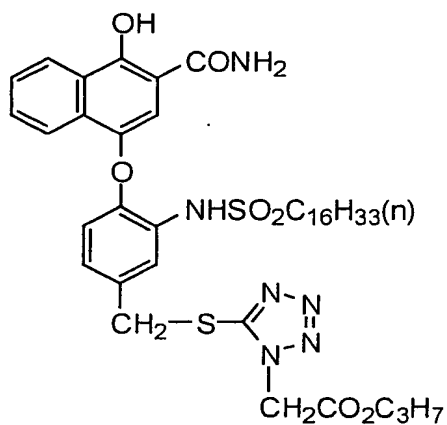
II-10



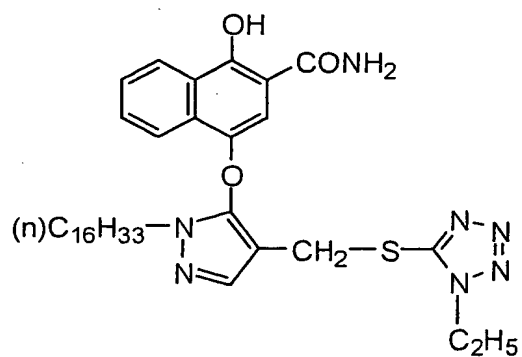
II-11



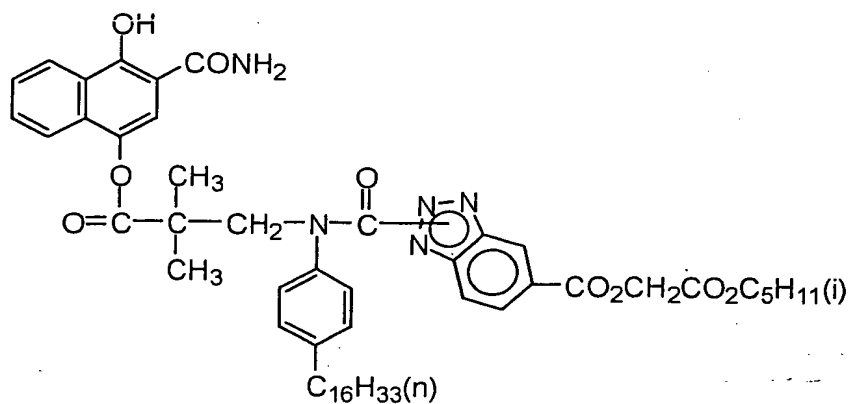
II-12



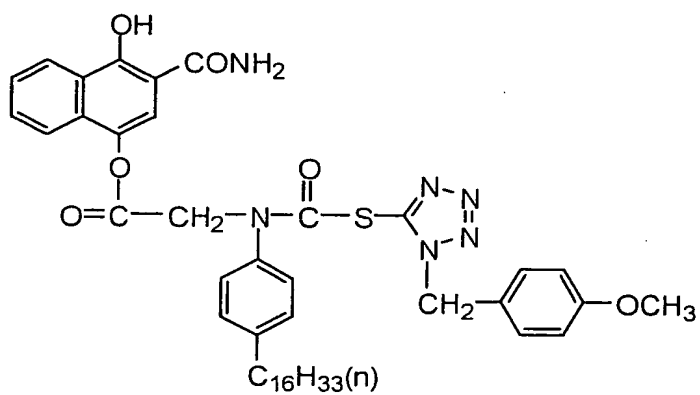
II-13



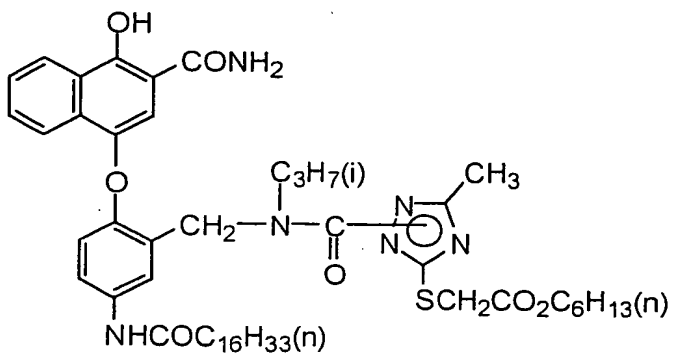
II-14



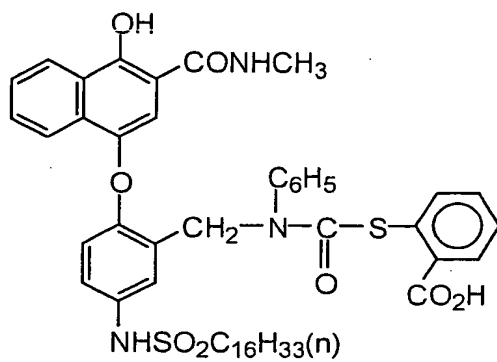
II-15



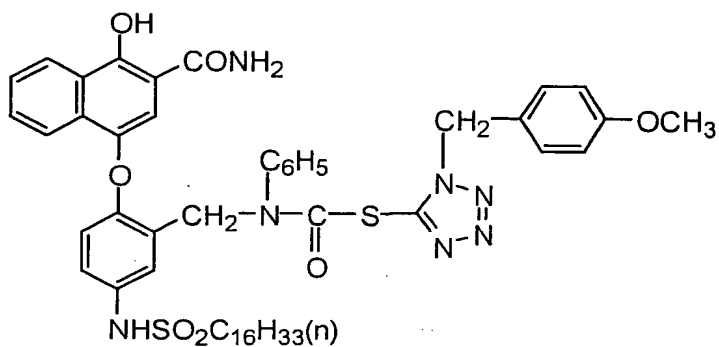
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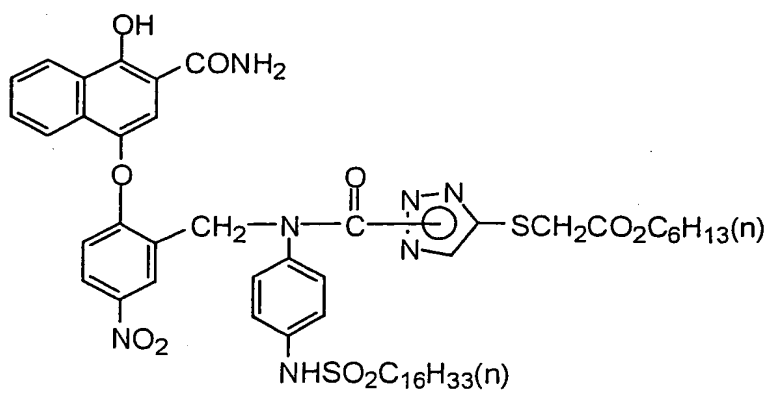
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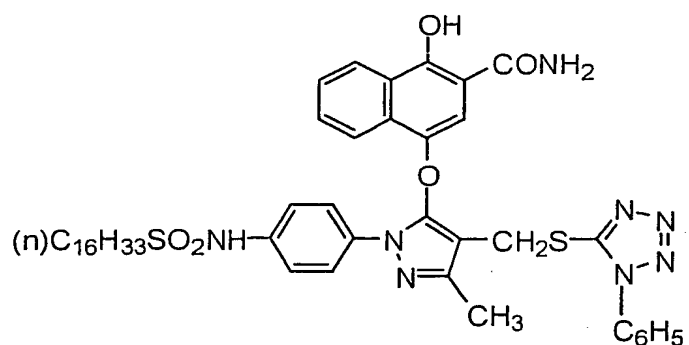
II-18



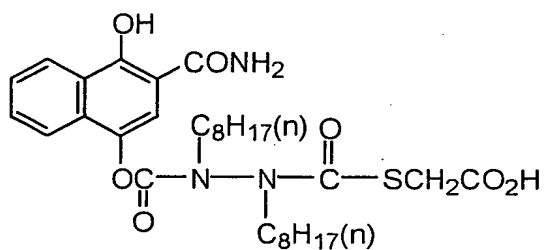
II-19



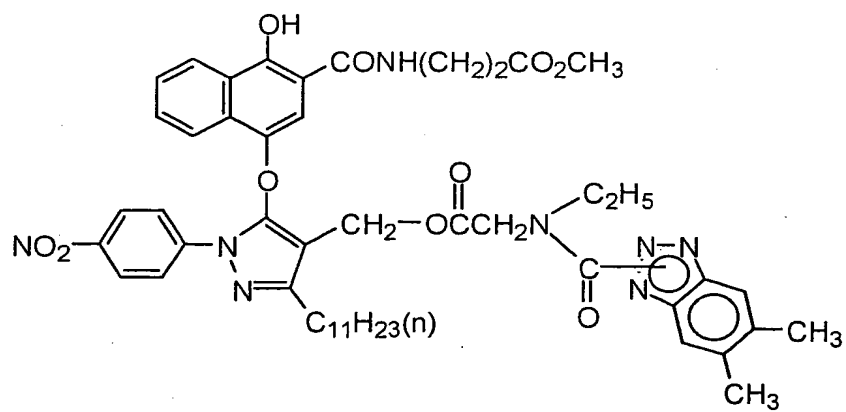
II-20



II-21

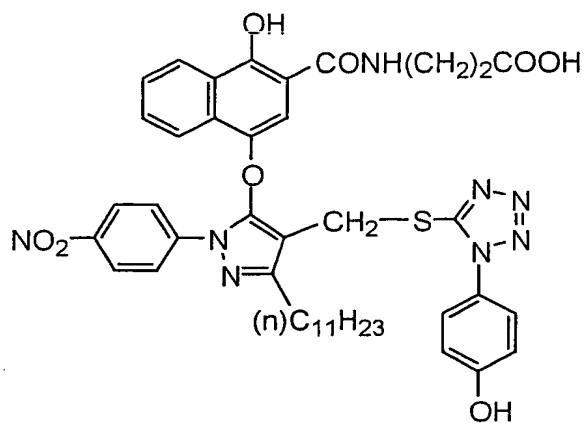


II-22

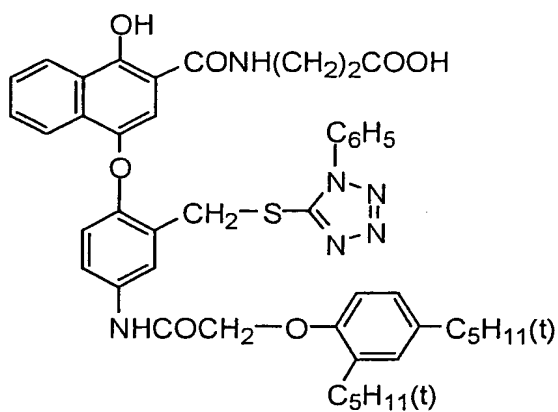




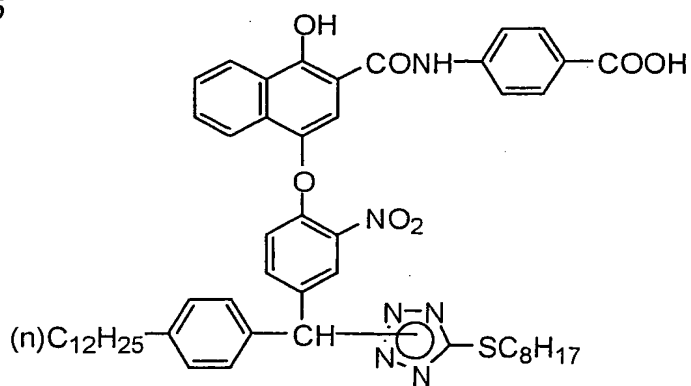
II-23



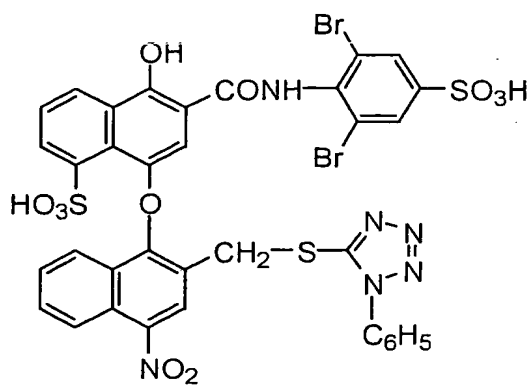
II-24



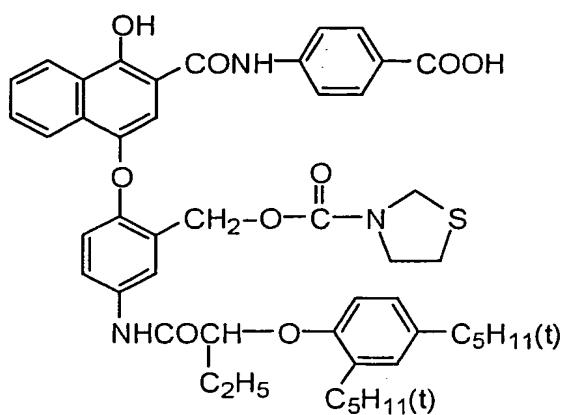
II-25



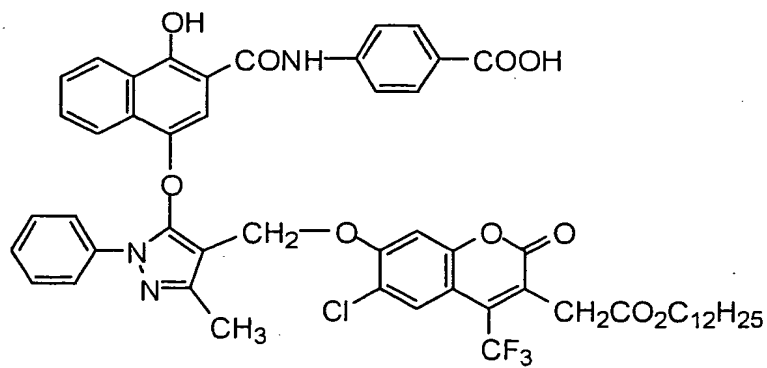
II-26

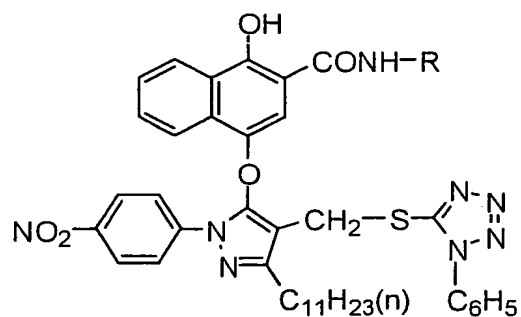


II-27



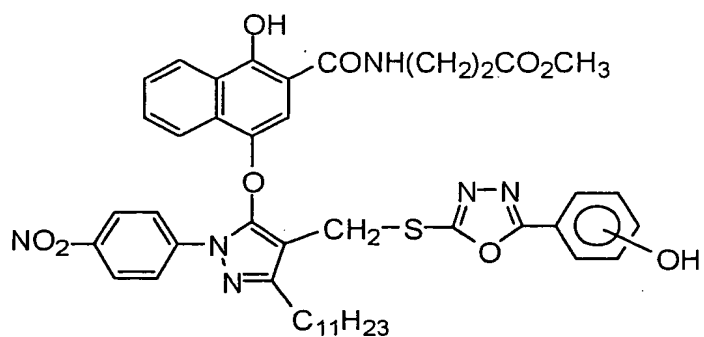
II-28



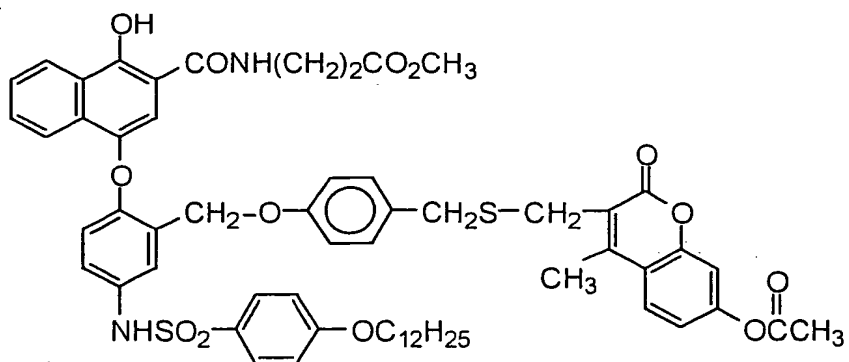


No.	R	No.	R
II - 29	$-(\text{CH}_2)_2\text{CO}_2\text{CH}_3$	II - 31	$-\text{CHCO}_2\text{CH}_3$ $\quad \quad \quad \text{CH}(\text{CH}_3)\text{C}_2\text{H}_5$
II - 30	$-(\text{CH}_2)_2\text{CO}_2\text{C}_4\text{H}_9(\text{n})$	II - 32	$-(\text{CH}_2)_4\text{CO}_2\text{CH}_3$

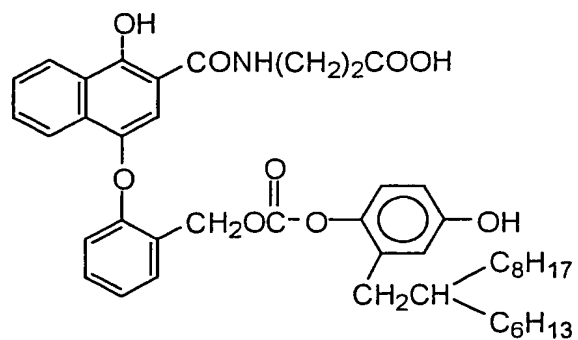
II - 33



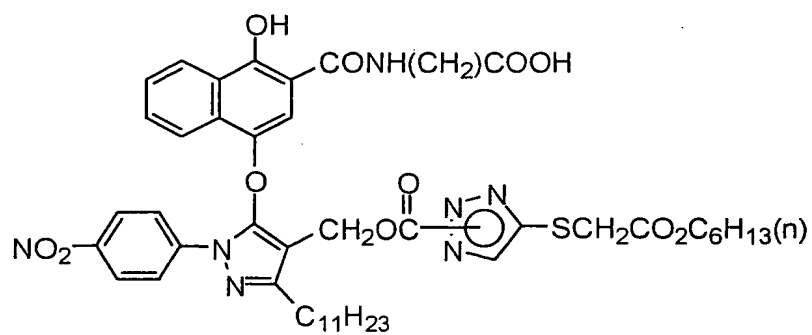
II - 34



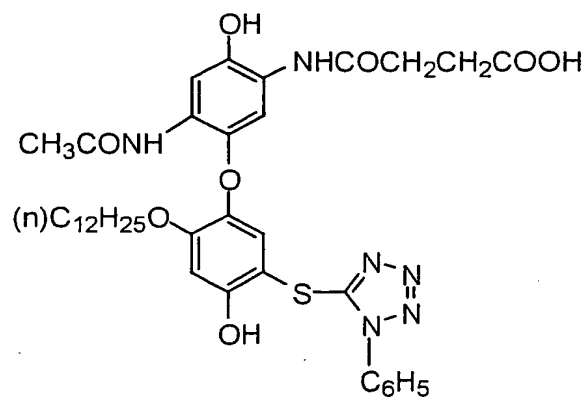
II-35



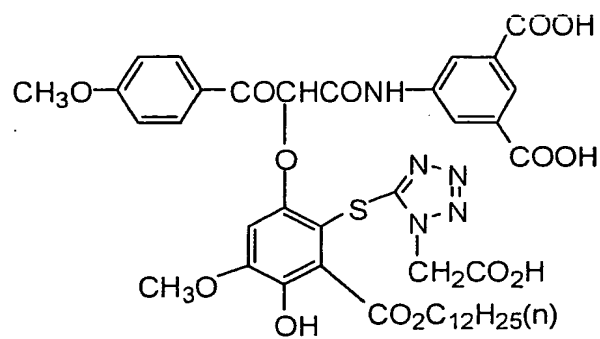
II-36



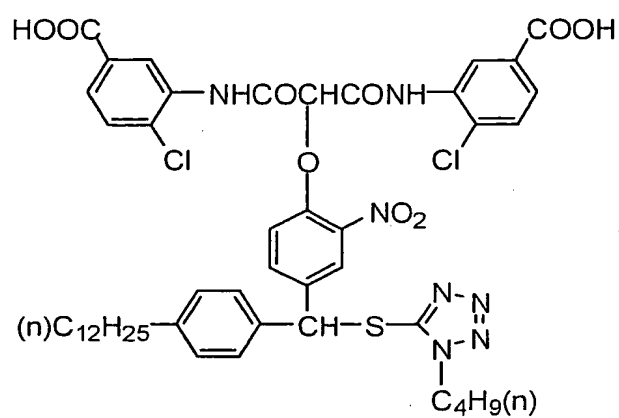
II-37



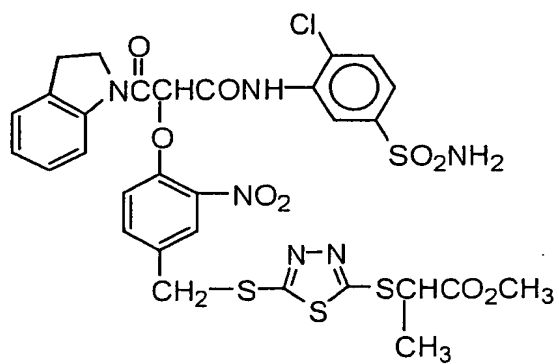
II-38



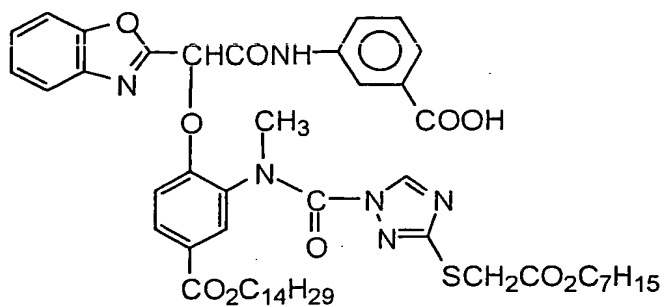
II-39



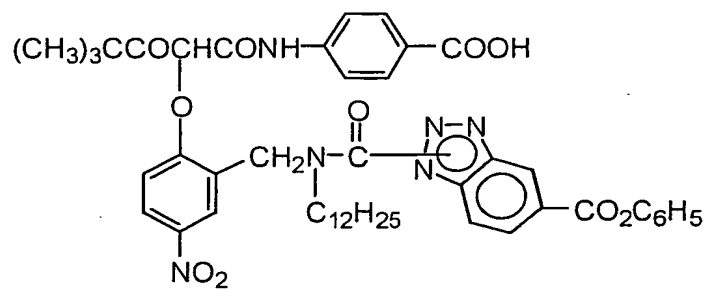
II-40



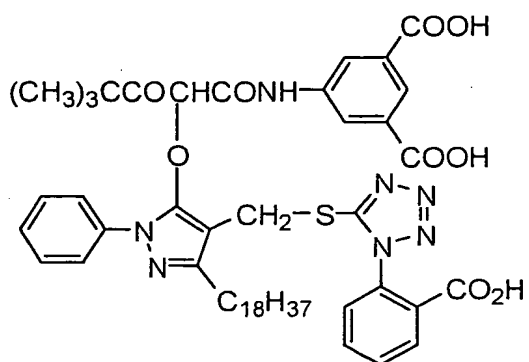
II-41



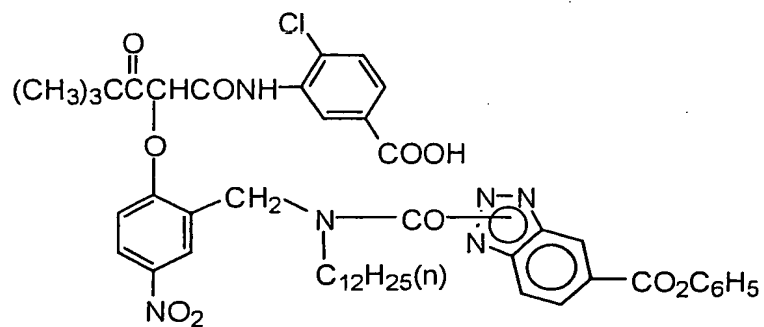
II-42



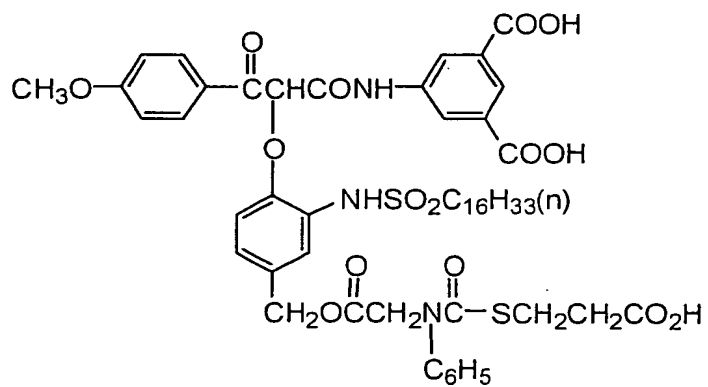
II-43



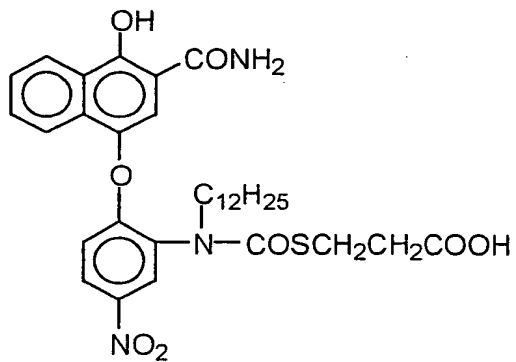
II-44

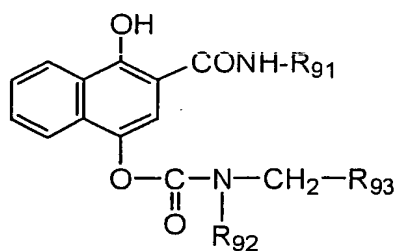


II-45



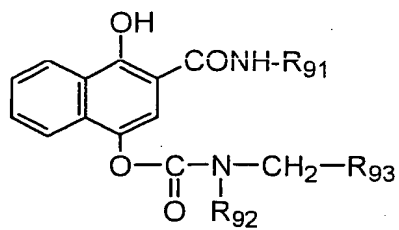
II-46







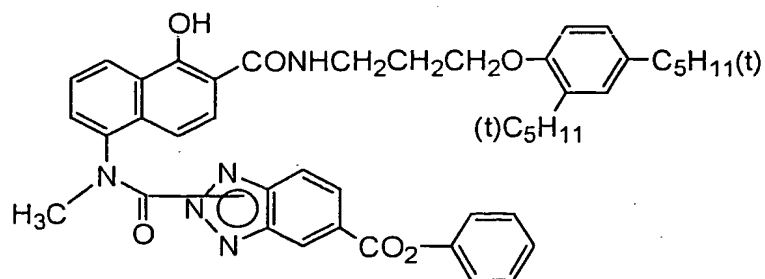
No.	R <sub>91</sub>	R <sub>92</sub>	R <sub>93</sub>
II -47	H	-CH <sub>2</sub> CO <sub>2</sub> C <sub>10</sub> H <sub>21</sub> (n)	
II -48	H	-NHSO <sub>2</sub> C <sub>12</sub> H <sub>25</sub> (n)	
II -49	-CH <sub>3</sub>	-CH <sub>2</sub> CO <sub>2</sub> C <sub>12</sub> H <sub>25</sub> (n)	
II -50	-CH <sub>3</sub>	-C <sub>8</sub> H <sub>17</sub> (n)	
II -51	-(CH <sub>2</sub> ) <sub>2</sub> OCH <sub>3</sub>	-CH <sub>2</sub> CO <sub>2</sub> C <sub>10</sub> H <sub>21</sub> (n)	
II -52	-(CH <sub>2</sub> ) <sub>2</sub> COOH	-(CH <sub>2</sub> ) <sub>3</sub> O--C <sub>5</sub> H <sub>11</sub> (t)	
II -53	-(CH <sub>2</sub> ) <sub>2</sub> COOH	-CH <sub>2</sub> --OC <sub>4</sub> H <sub>9</sub>	



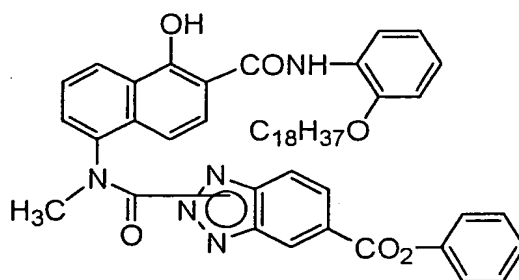


No.	R <sub>91</sub>	R <sub>92</sub>	R <sub>93</sub> R <sub>93</sub>
II -54	-SO <sub>2</sub> CH <sub>3</sub>	-CH <sub>2</sub> CO <sub>2</sub> C <sub>10</sub> H <sub>21</sub> (n)	
II -55	-COCH <sub>3</sub>	-C <sub>12</sub> H <sub>25</sub> (n)	
II -56	-CO-  -COOH	-C <sub>10</sub> H <sub>21</sub> (n)	
II -57	-SO <sub>2</sub> C <sub>4</sub> H <sub>9</sub> (n)	-CO <sub>2</sub> C <sub>12</sub> H <sub>25</sub> (n)	
II -58	H	 -C <sub>8</sub> H <sub>17</sub> (t)	
II -59	-(CH <sub>2</sub> ) <sub>2</sub> CO <sub>2</sub> CH <sub>3</sub>	-CO <sub>2</sub> C <sub>10</sub> H <sub>21</sub> (n)	

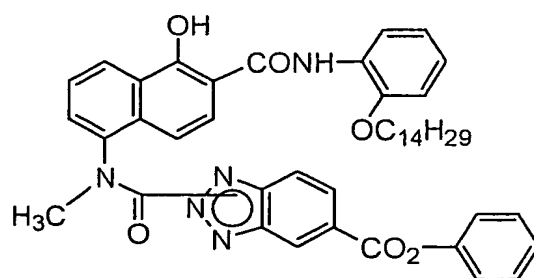
II-60



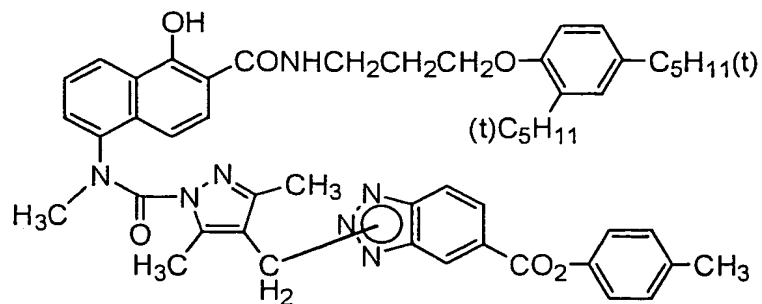
II-61



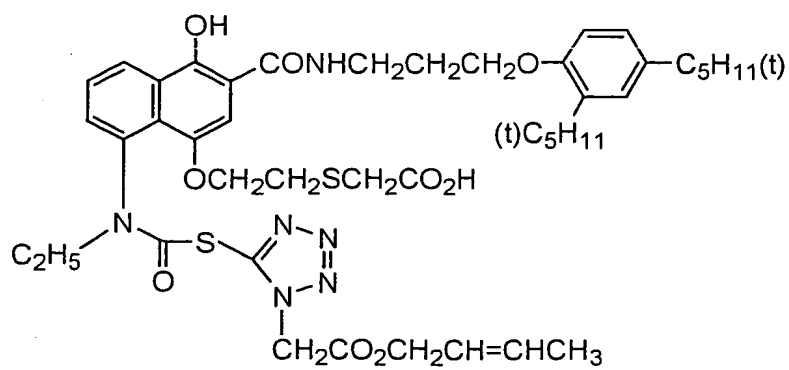
II-62



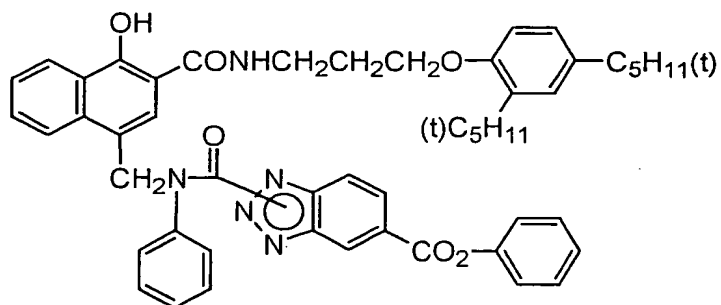
II-63



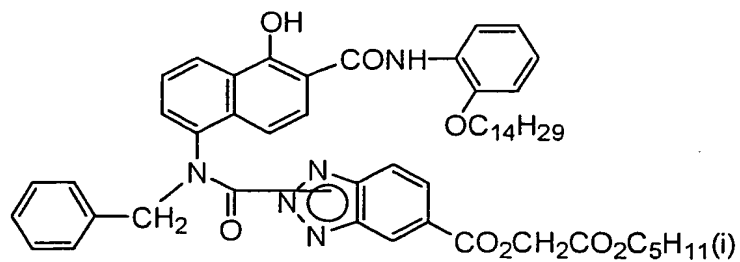
II-64



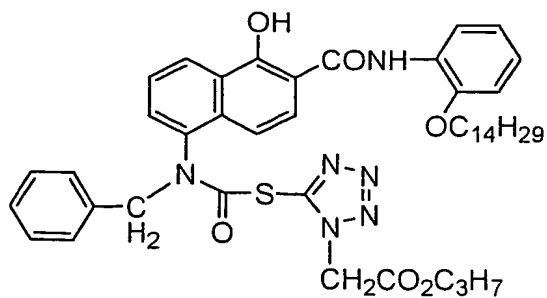
II-65



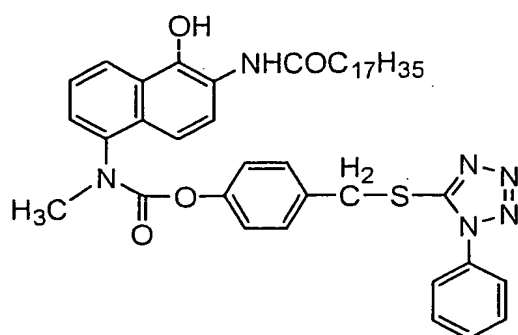
II-66



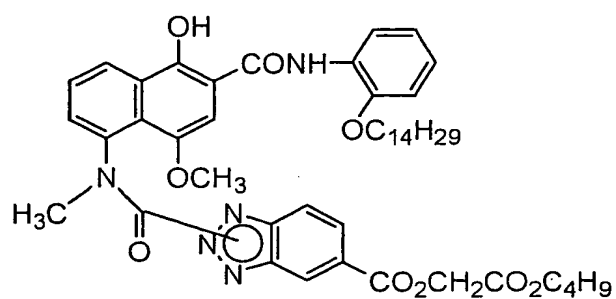
II-67



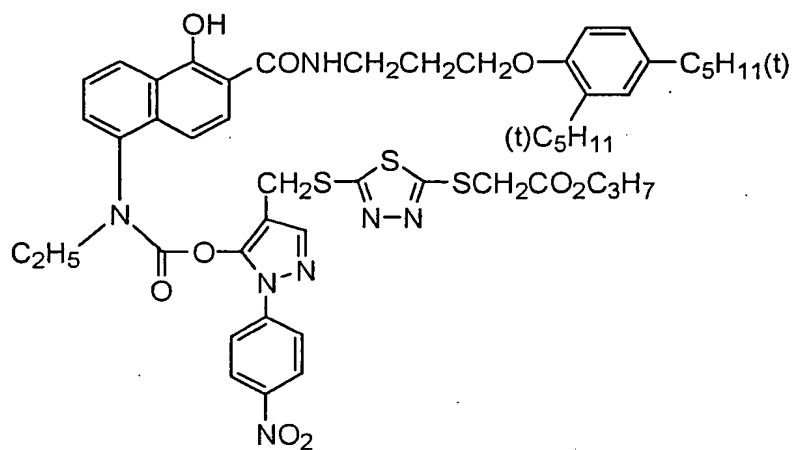
II-68



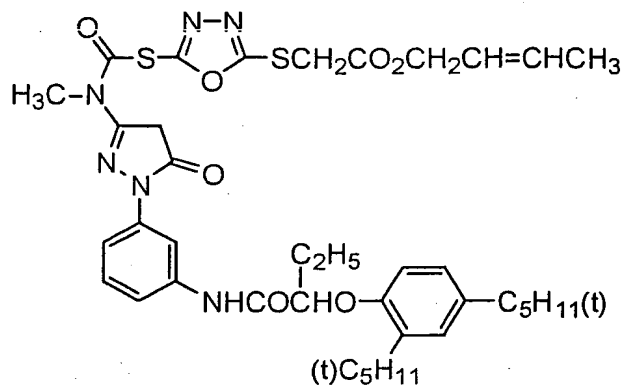
II-69



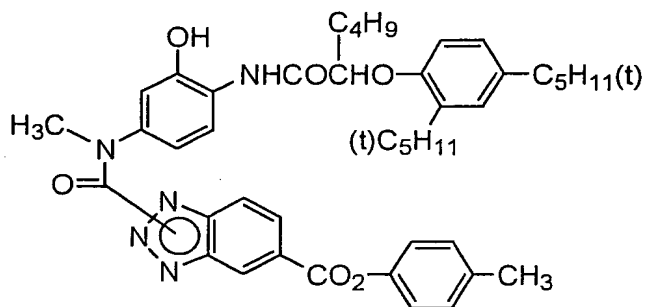
II-70



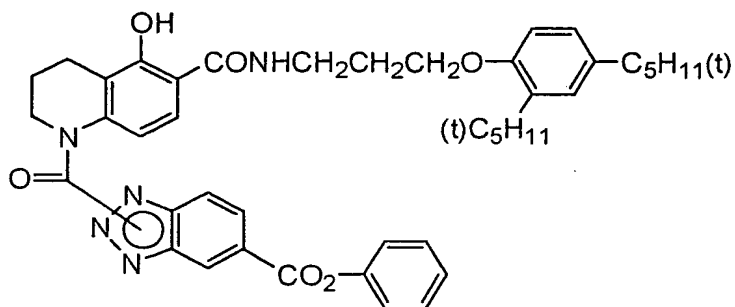
II-71



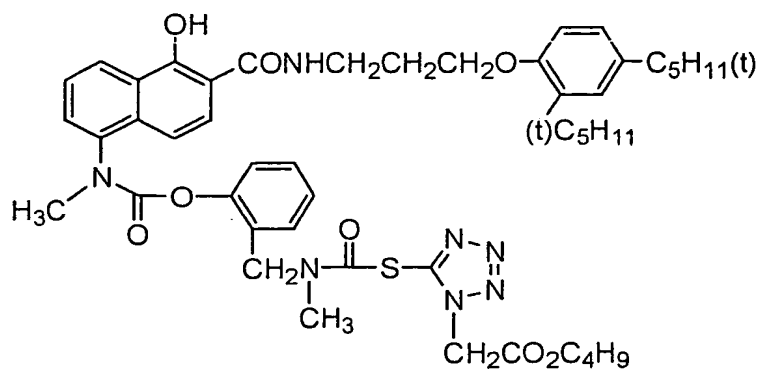
II-72



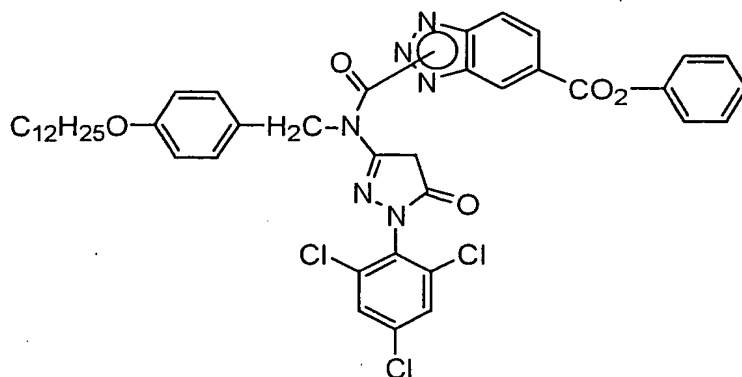
II-73



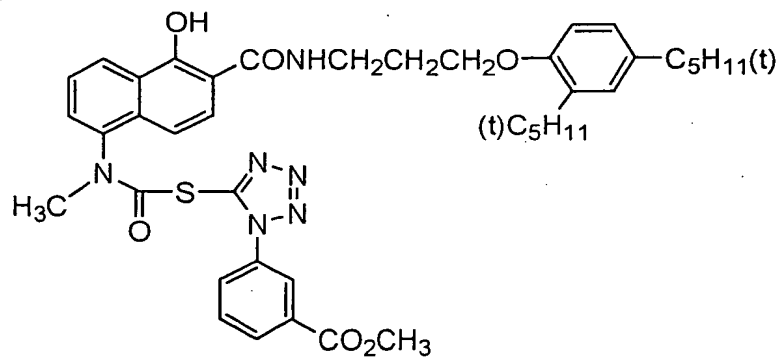
II-74



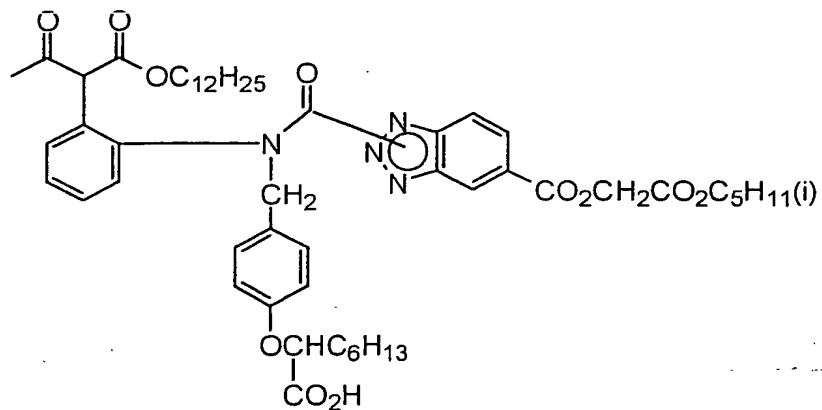
II-75



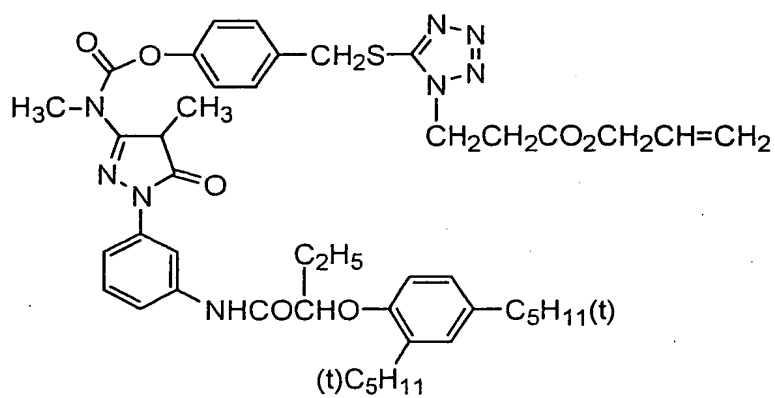
II-76



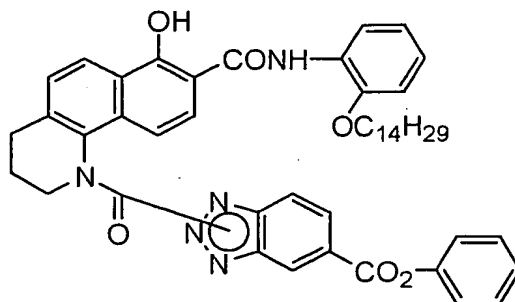
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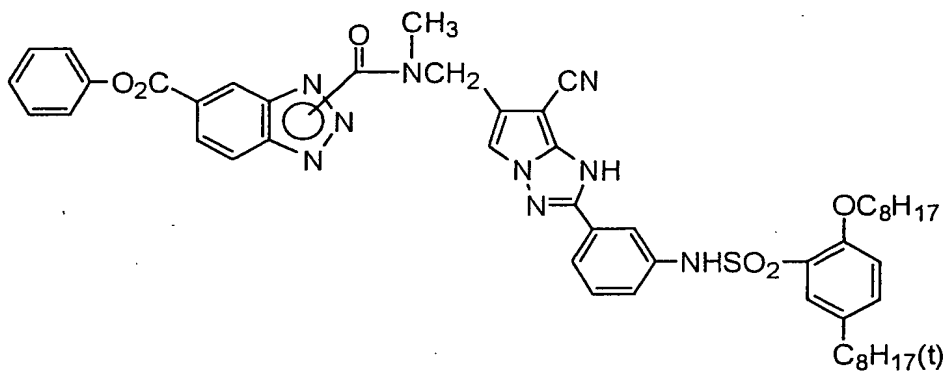
II-78



II-79

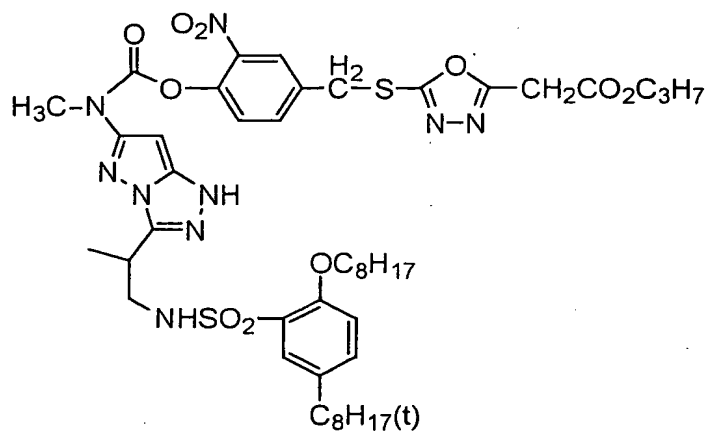


II-81

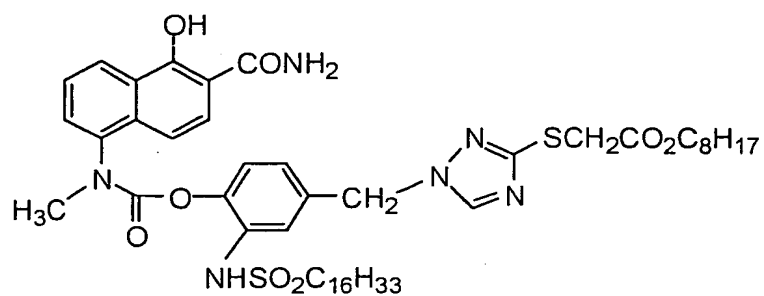
CCCCCCCCCCCC(=O)Nc1ccc(cc1C2=NC(=NC3=C2N=CN3C(C)=C(C)C)N)C(=O)NCCc2ccccc2C(=O)SC3=NN=NN3C(=O)OCCF



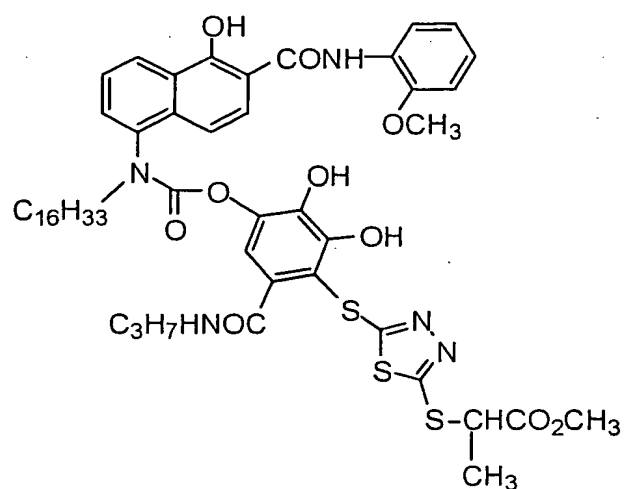
II-84

CCCCCCCCCCCCCCCCN(C(=O)N1C=NC2=C(C=C1)C(=C(C=C2)C(=O)OC3=CC=CC=C3)C4=CC=C(C=C4)C(=O)Nc5ccc(NC(=O)C)cc5)c6c(O)c7ccccc67

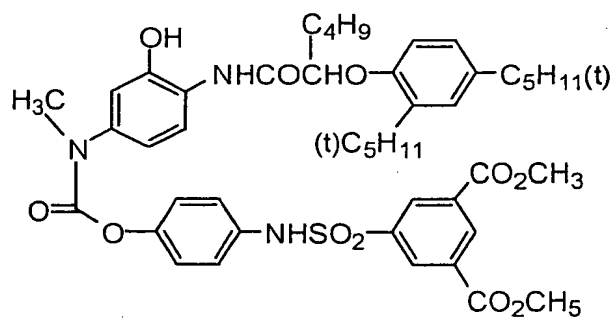
II-86



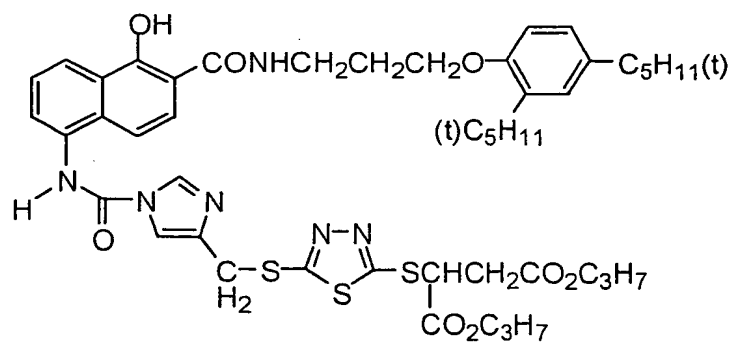
II-87



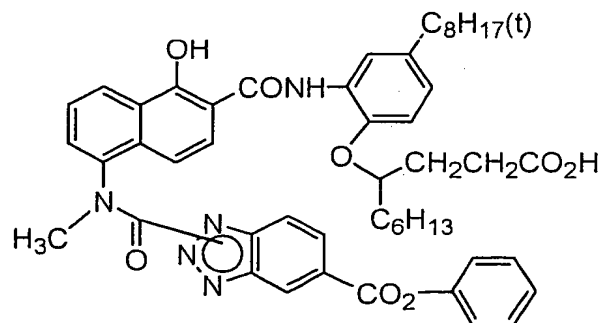
II-88



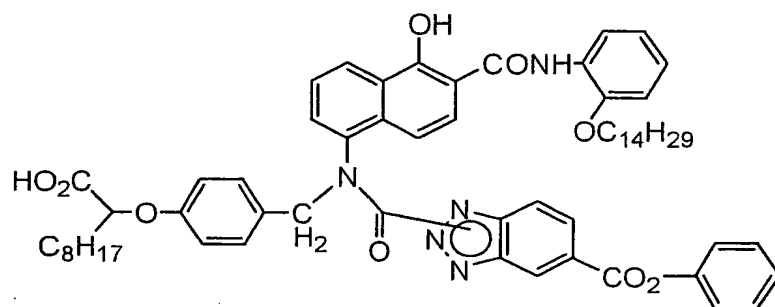
II-89



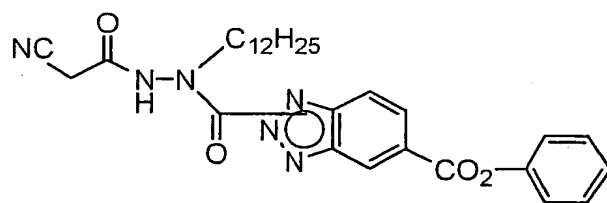
II-90



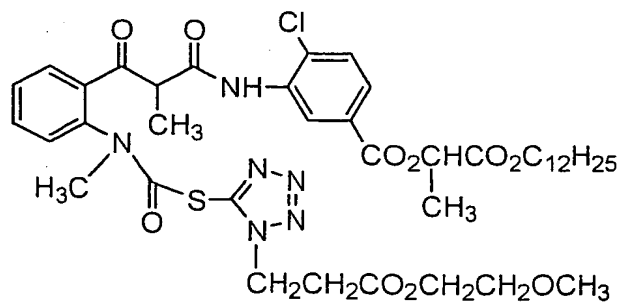
II-91



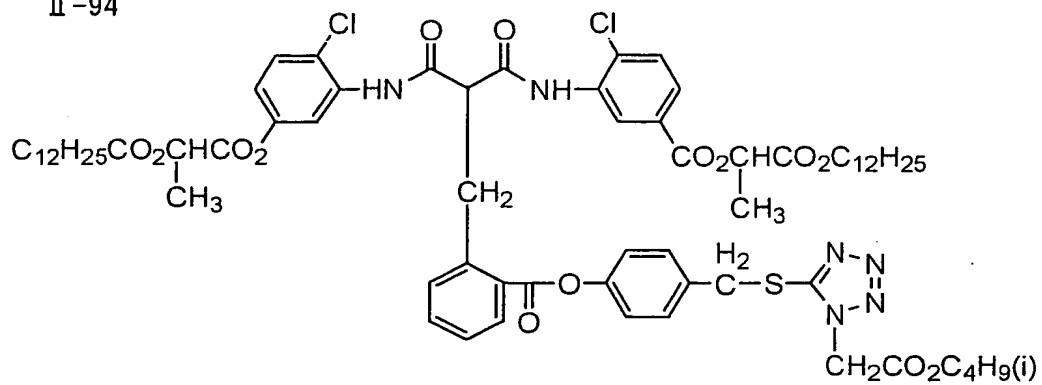
II-92



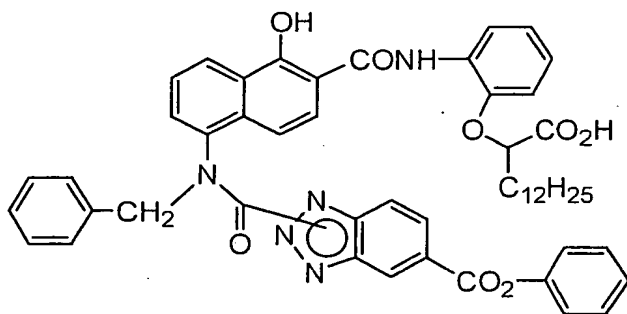
II-93



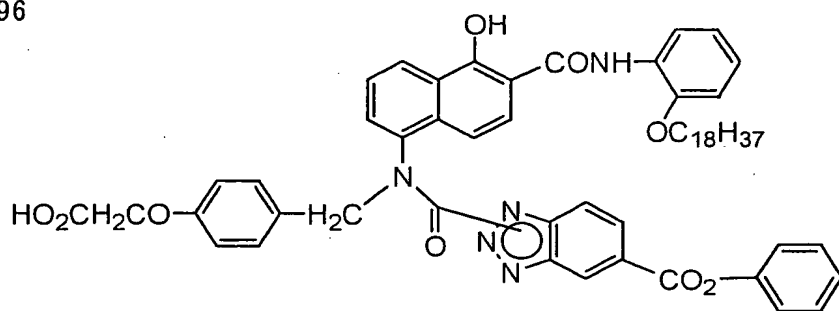
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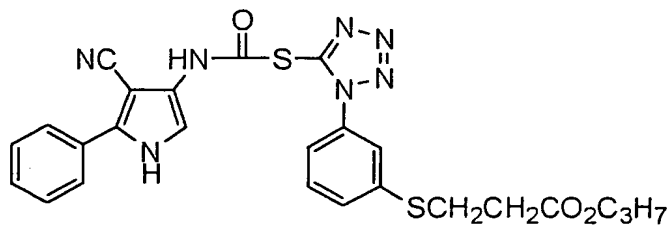
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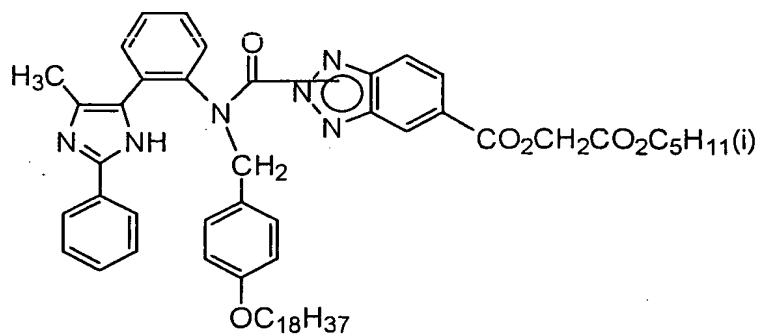
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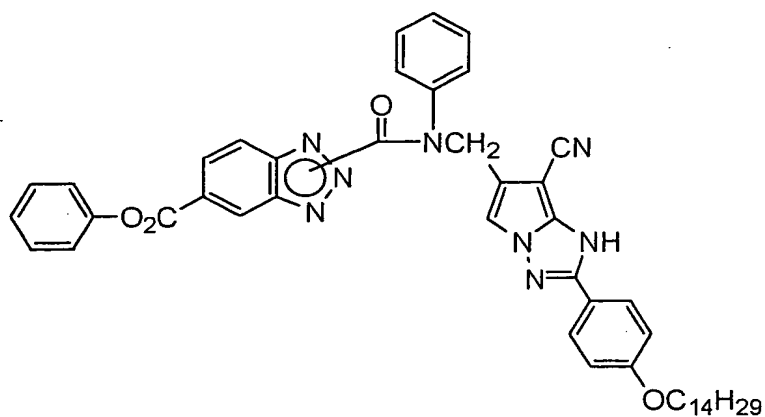
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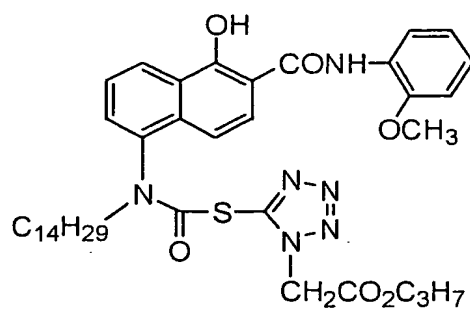
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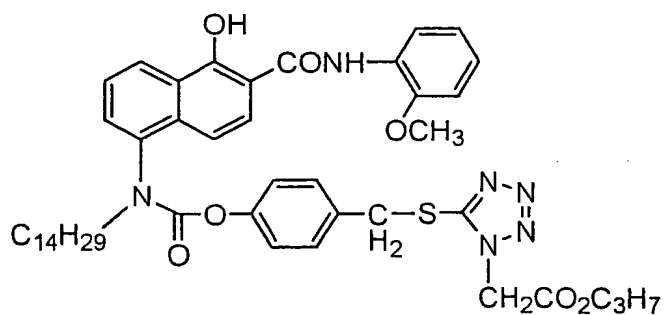
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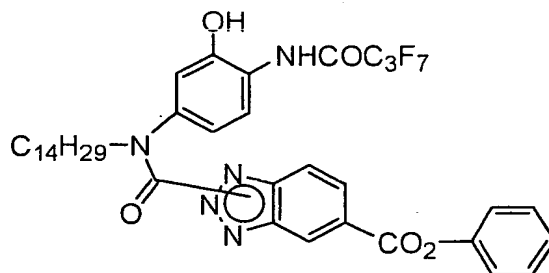
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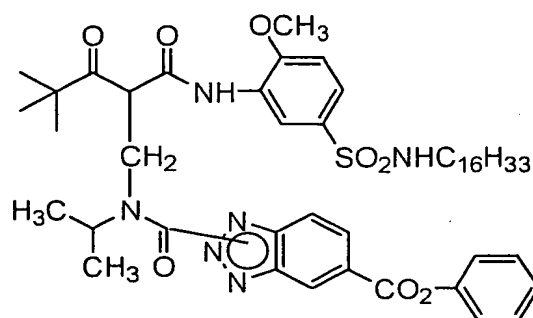
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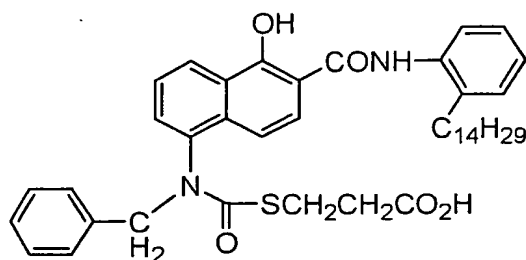
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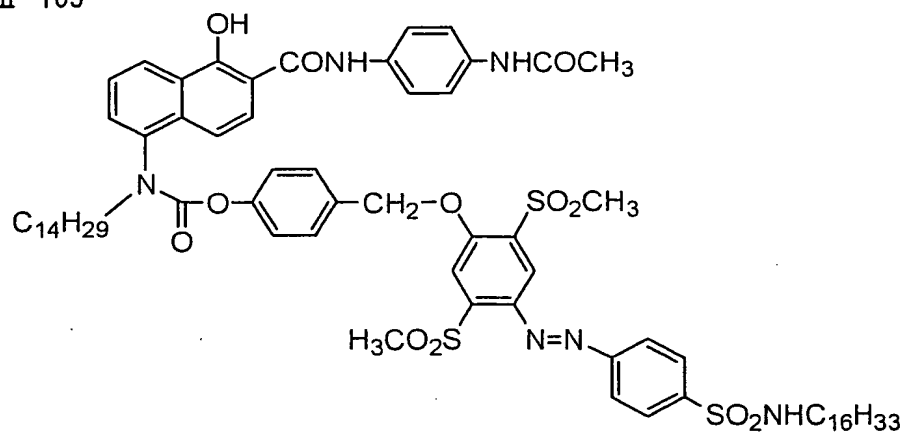
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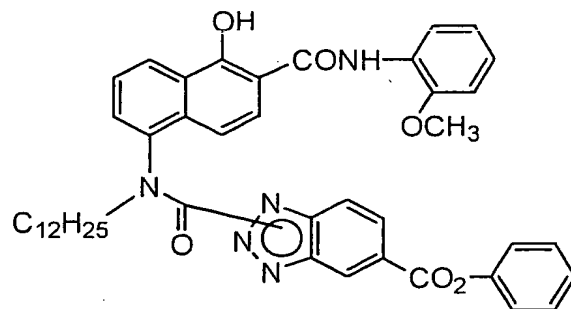
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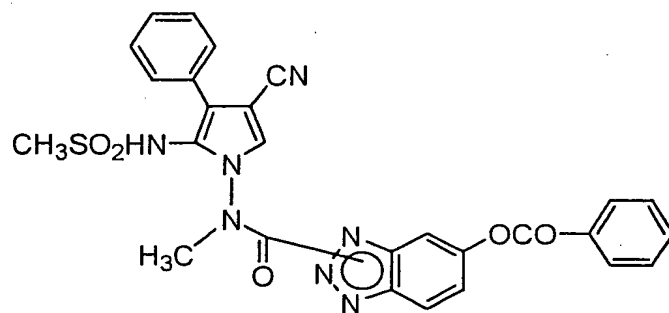
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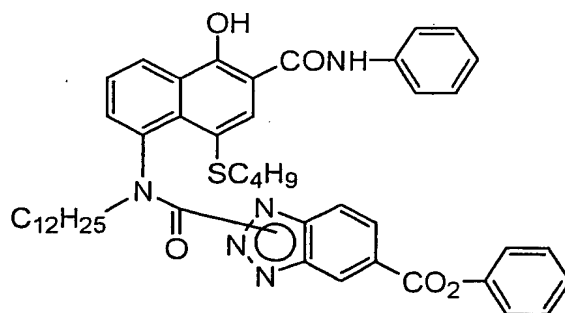
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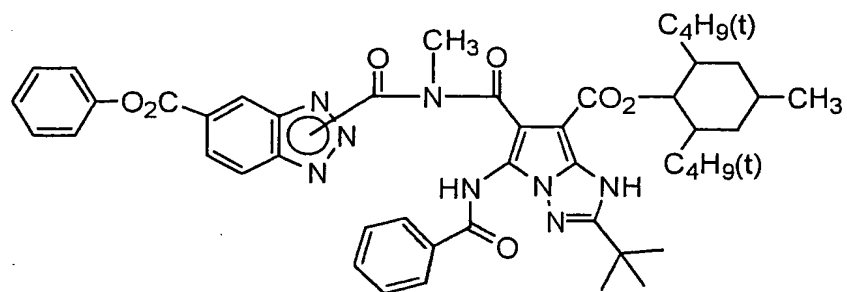
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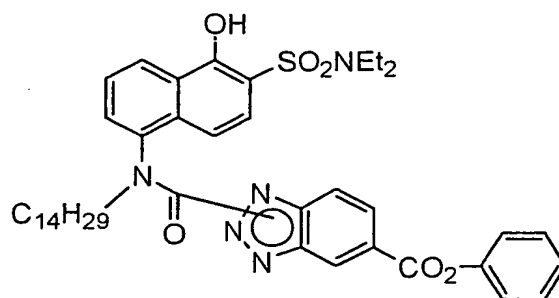
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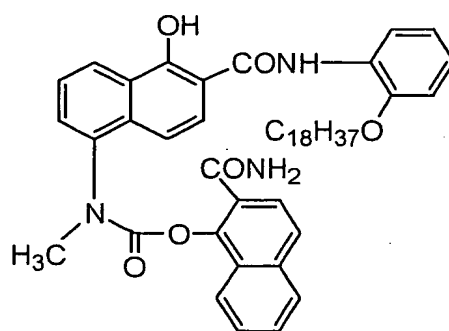
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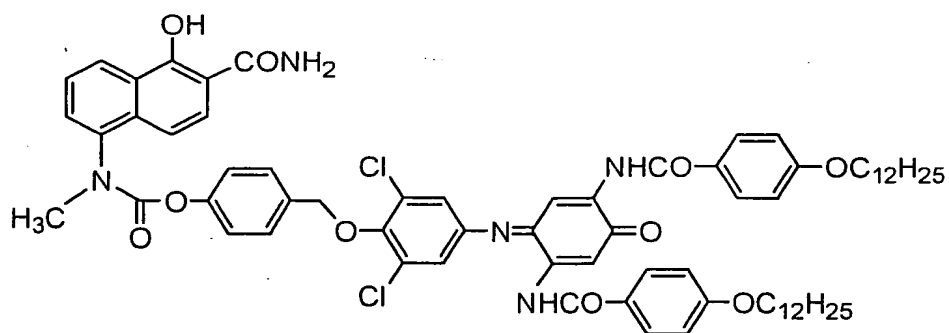
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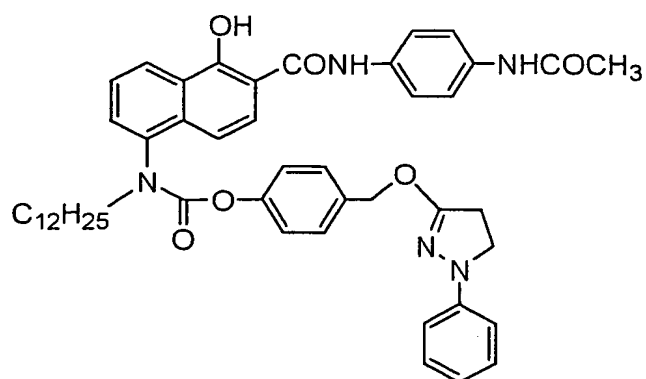
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II-112

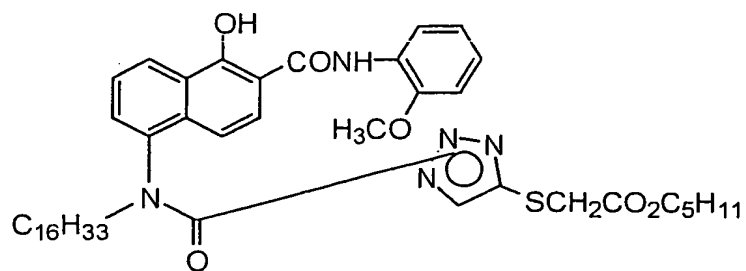


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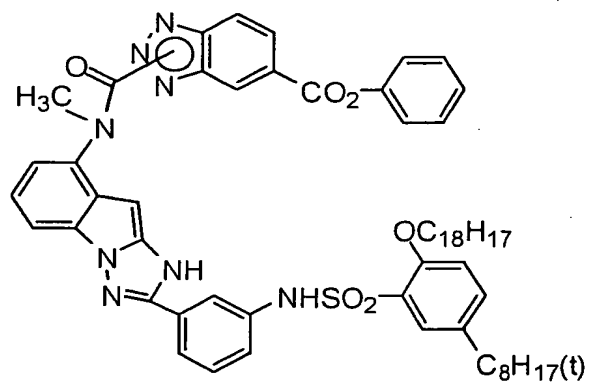




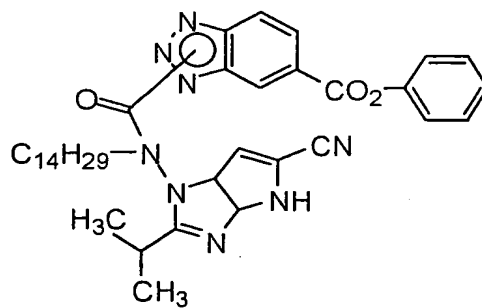
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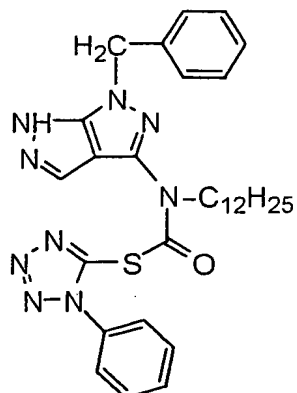
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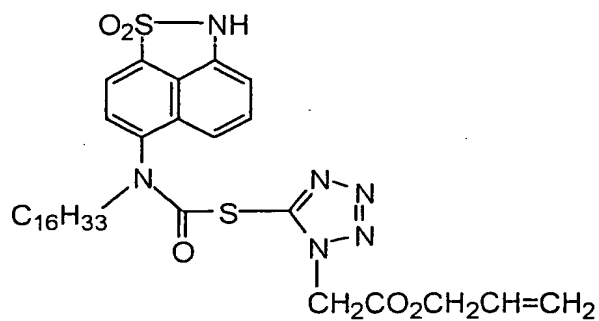
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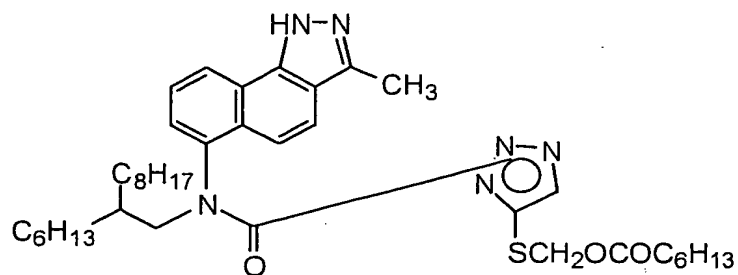
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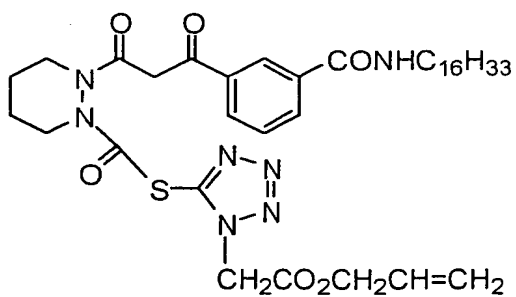
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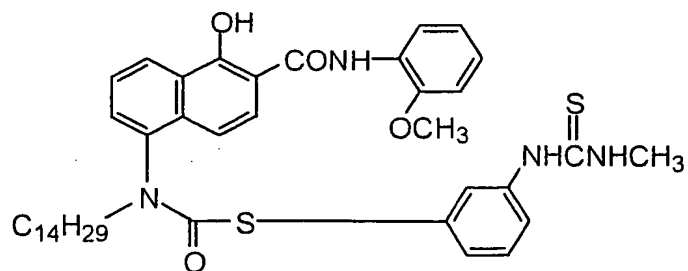
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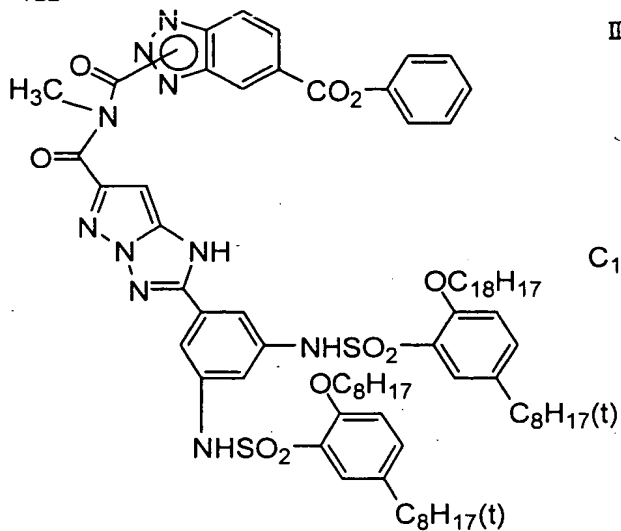
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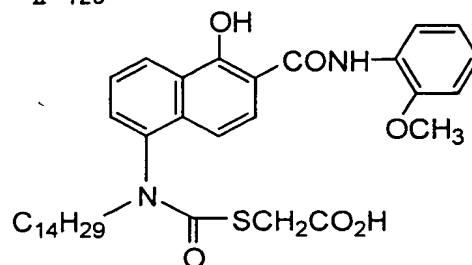
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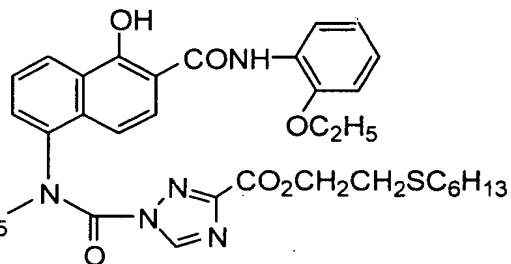
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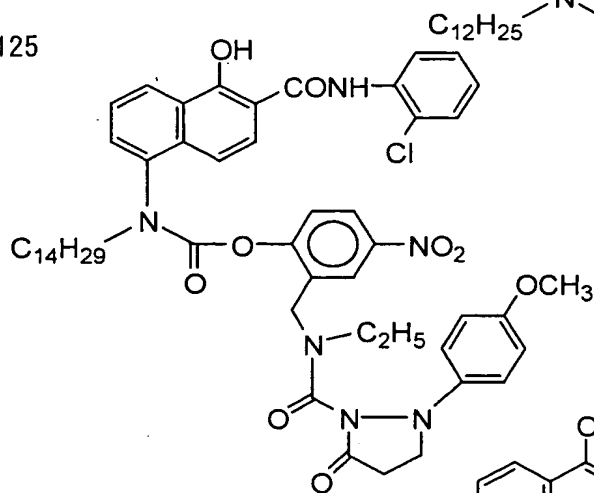
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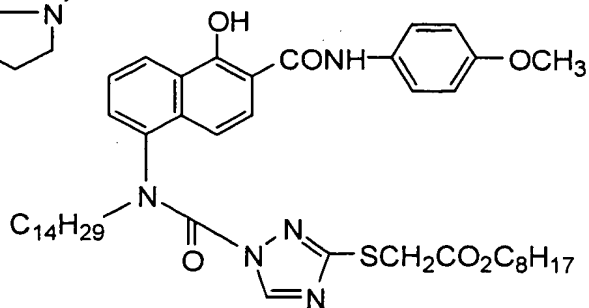
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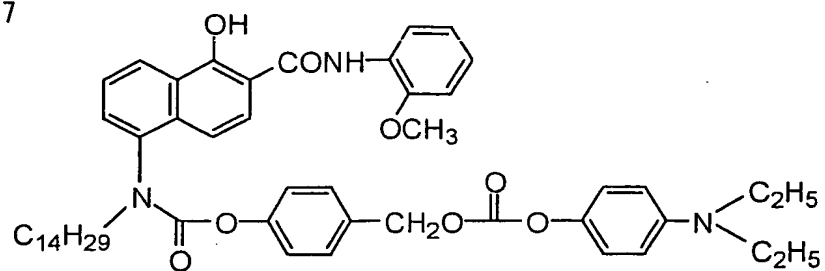
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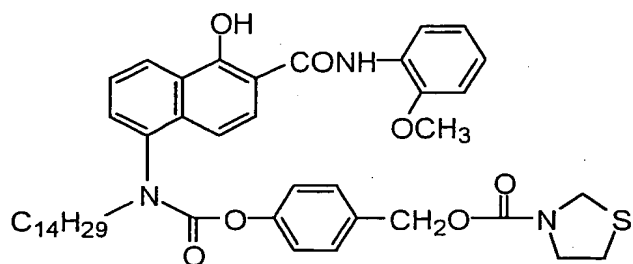
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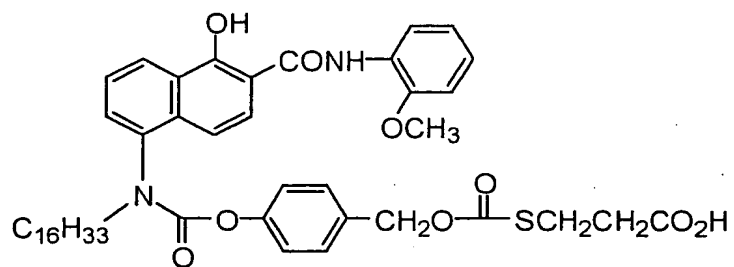
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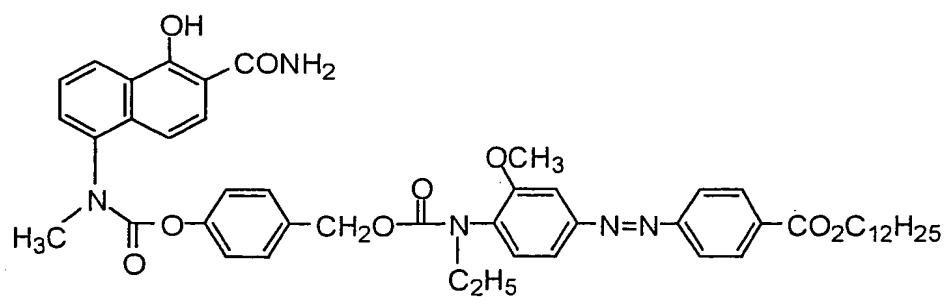
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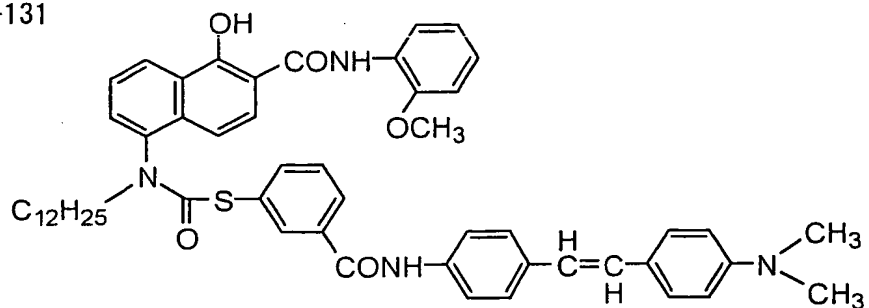
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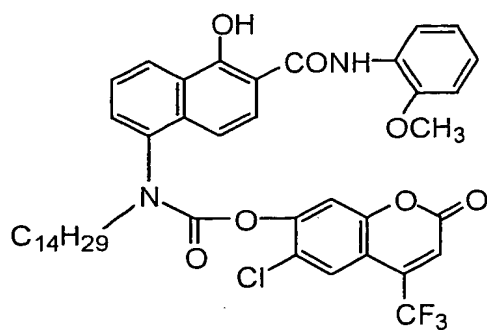
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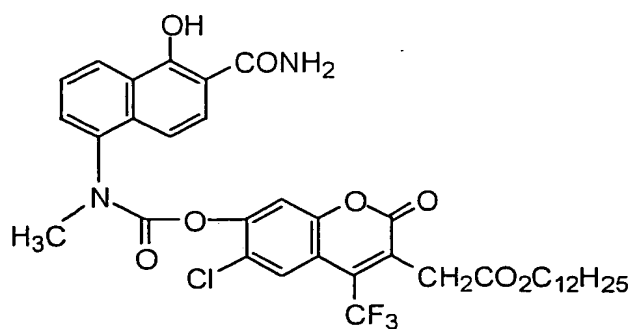
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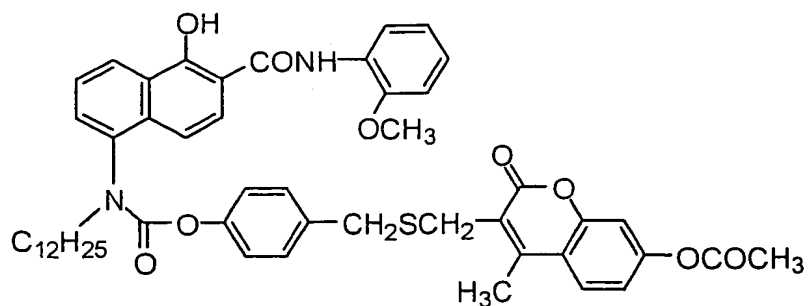
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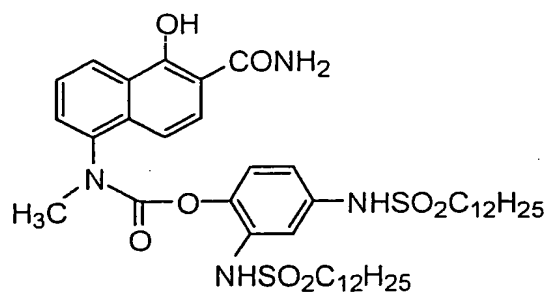
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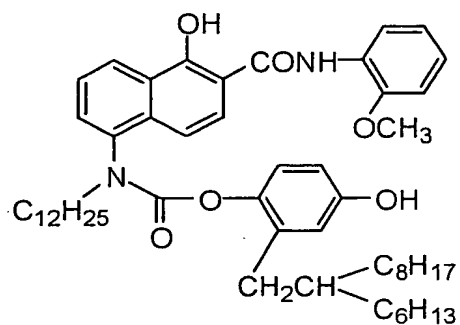
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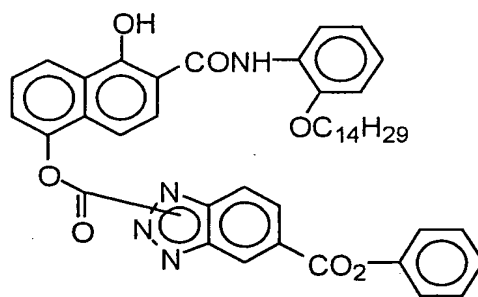
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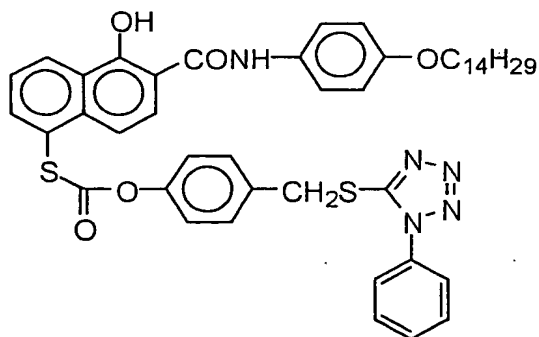
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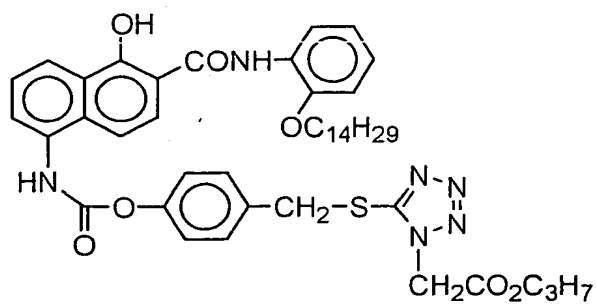
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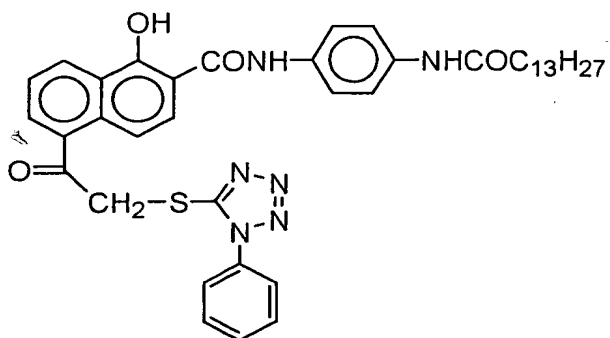
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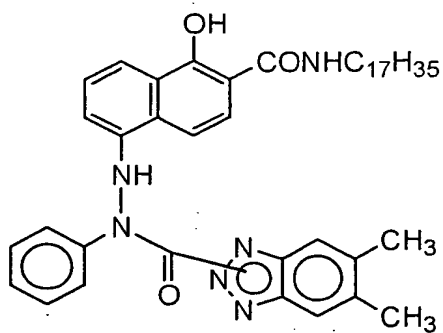
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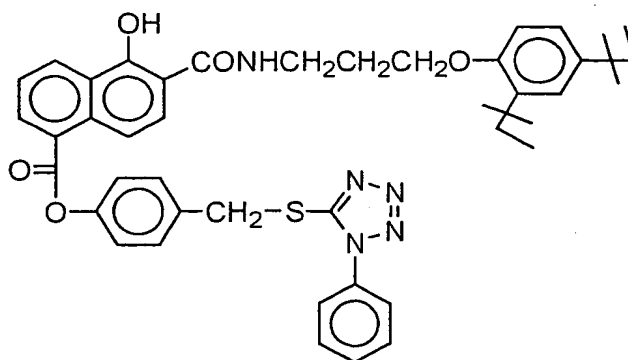
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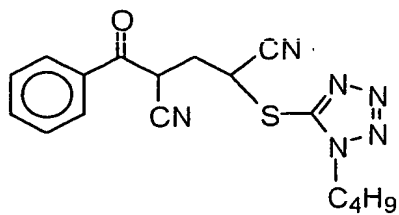
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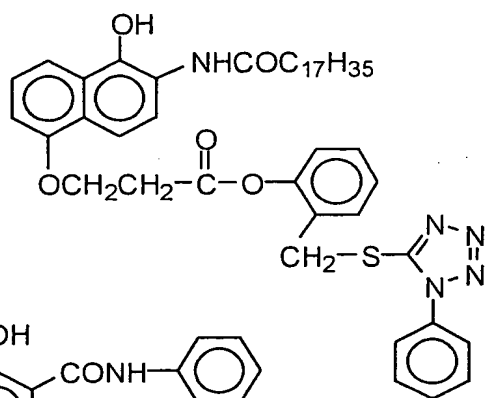
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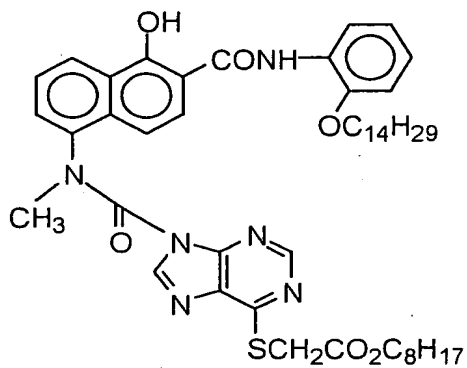
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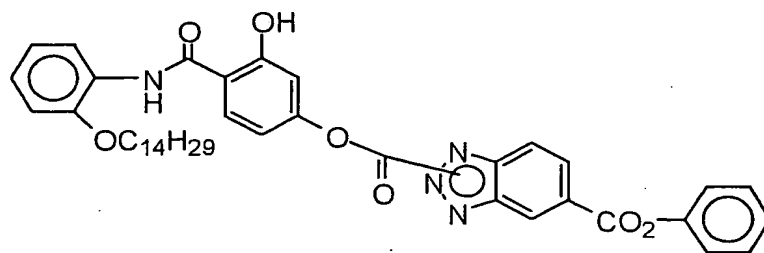
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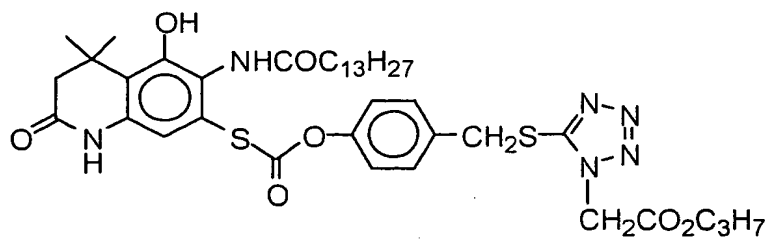
II-145



II-146

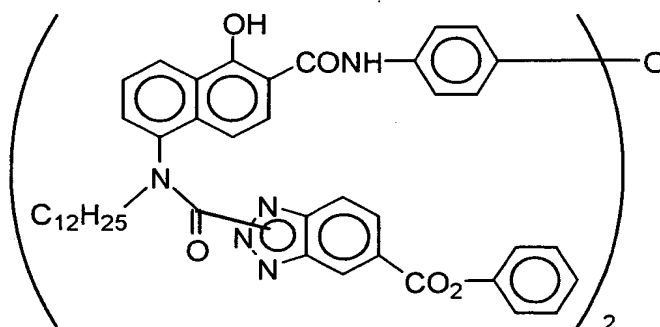


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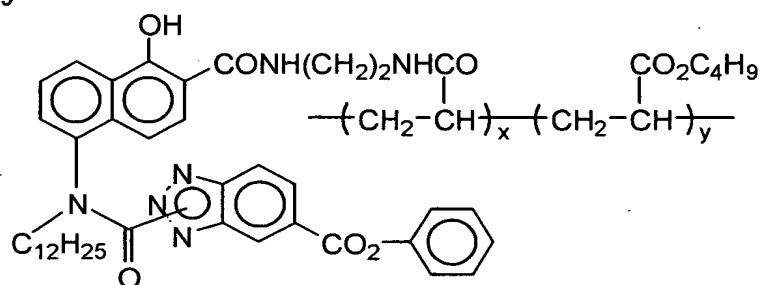




II-148



II-149

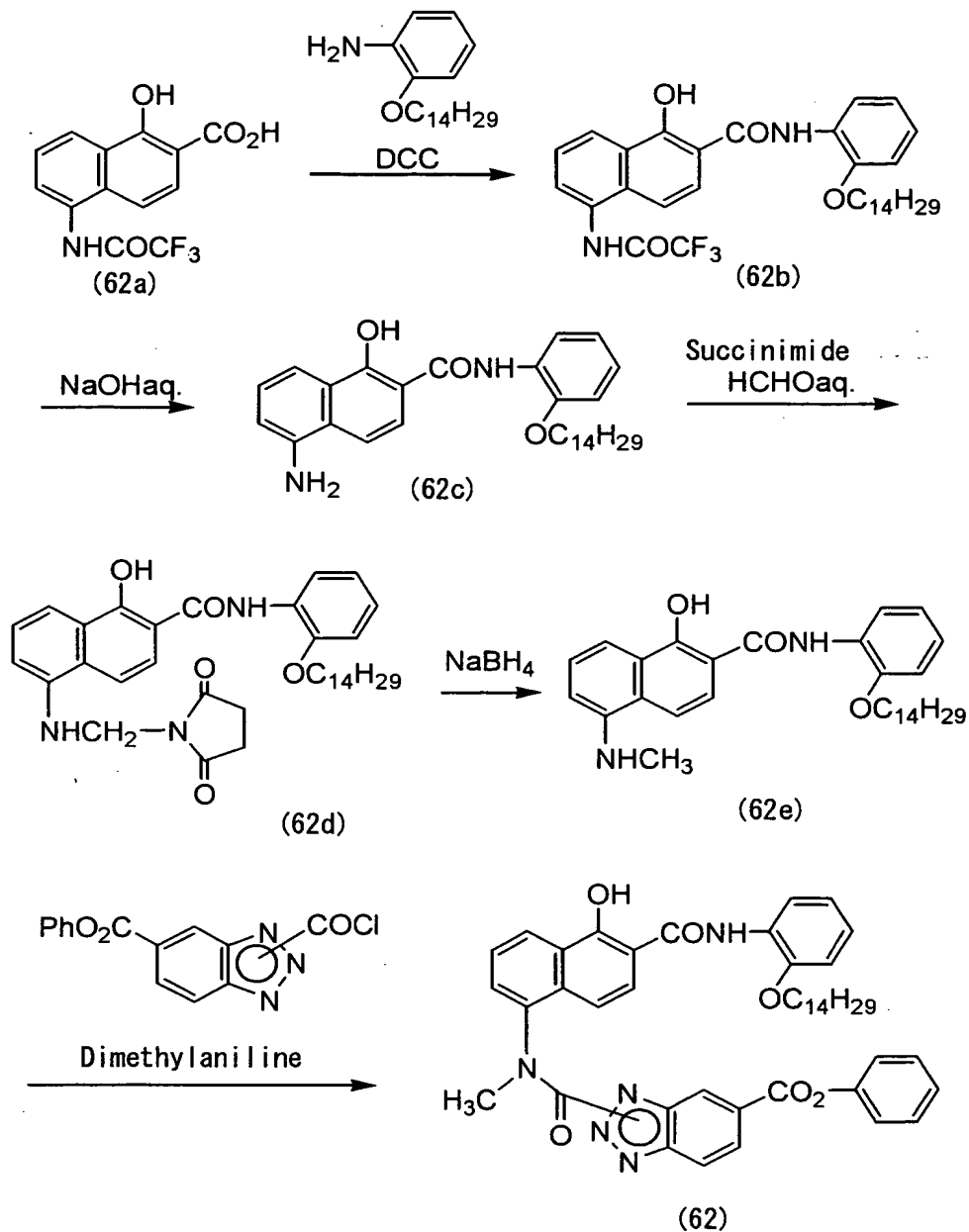


$x : y = 70 : 30$  (molar ratio)

Synthesis methods of the compounds represented by general formula (III) are described, for example, in JP-A's-58-162949, 63-37350, 4-356042, 5-61160, and 6-130594, and U.S.P. No. 5,234,800.

An example of a synthesis method of a compound represented by the general formula (III) is set forth below.

Synthesis of coupler, exemplified compound (62)



An N,N-dimethylacetamide (60 milliliters (to be referred to as "mL" hereinafter) solution of dicyclohexylcarbodiimide (41.3g) was dropped into an N,N-dimethylacetamide (250 mL) solution of a compound 62a (50g) and o-tetradecyloxyaniline (51.1g) at 30°C.

After the reaction solution was stirred at 50°C for 1 hr, ethyl acetate (250 mL) was added, and the resultant solution was cooled to 20°C. The reaction solution was filtered by suction, and 1N hydrochloric acid aqueous solution (250 mL) was added to the filtrate to separate it. Hexane (100 mL) was added to the organic layer, and the separated crystals were filtered out, washed with acetonitrile, and dried to obtain a compound 62b (71g).

10      Synthesis of compound 62c

          An aqueous solution (150 mL) of sodium hydroxide (30g) was dropped into a methanol (350 mL)/tetrahydrofuran (70 mL) solution of the compound 62b (71g). The resultant solution was stirred in a nitrogen atmosphere at 60°C for 1 hr. After the reaction solution was cooled to 20°C, concentrated hydrochloric acid was dropped until the system became acidic. The separated crystals were filtered out, washed with water and followed by acetonitrile, and dried to obtain a compound 62c (63g).

20      Synthesis of compound 62d

          An ethanol solution (150 mL) of the compound 62c (20g), succinic acid imide (5.25g), and an aqueous 37% formalin solution (4.3 mL) was stirred under reflux for 5 hrs. After the resultant solution was cooled to 20°C, the separated crystals were filtered out and dried to obtain a compound 62d (16g).

Synthesis of compound 62e

Sodium boron hydride (1.32g) was slowly added to a dimethylsulfoxide (70 mL) solution of the compound 62d (7g) at 60°C such that the temperature did not  
5 exceed 70°C. The resultant solution was stirred at the same temperature for 15 min. After the reaction solution was slowly added to 1N hydrochloric acid aqueous solution (100 mL), ethyl acetate (100 mL) was added for extraction. The organic layer was washed  
10 with water, dried by magnesium sulfate, and condensed at reduced pressure. After a placing point component was removed by a short-passage column (developing solvent: ethyl acetate/hexane = 2/1), the resultant material was recrystallized from the ethyl  
15 acetate/hexane system to obtain a compound 62e (3.3g).  
Synthesis of compound (62)

A dichloromethane (100 mL)/ethyl acetate (200 mL) solution of phenoxycarbonylbenzotriazole (4.78g) and N,N-dimethylaniline (2.42g) was dropped into  
20 a dichloromethane (80 mL) solution of bis(trichloromethyl) carbonate (1.98g). The resultant solution was stirred at 20°C for 2 hrs (solution S).

120 mL of this solution S were dropped into a tetrahydrofuran (20 mL)/ethyl acetate (20 mL) solution  
25 of the compound 62e (2.0g) and dimethylaniline (0.60g). The resultant solution was stirred at 20°C for 2 hrs. After the reaction solution was slowly added to 1N

hydrochloric acid aqueous solution (200 mL), ethyl acetate (200 mL) was added for extraction. The organic layer was washed with water, dried by magnesium sulfate, and concentrated at reduced pressure. The resultant material was purified through a column (developing solvent: ethyl acetate/hexane = 1/5) and recrystallized from the ethyl acetate/hexane system to obtain a compound example (62) weighing 1.3g (m.p. = 138 to 140°C) (the compound was identified by elementary analysis, NMR, and mass spectrum).

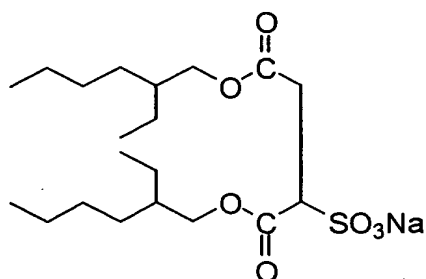
Although any surfactant having a critical micelle concentration of  $4.0 \times 10^{-3}$  mol/L or less can be used in the present invention, preferred are those which function as dispersing agents for high boiling organic solvents. More preferable surfactants for use in the present invention include anionic surfactants such as sulfoalkyl and sulfoaryl, nonionic surfactants such as alkyl polyethylene oxide, and betaine surfactants such as sulfoalkylammonium. Polymer surfactants comprising polymers with functional groups bonded can also be used. The critical micelle concentration used herein is defined as a concentration at which a concentration-surface tension curve reaches the minimum surface tension. The concentration-surface tension curve is obtained through a process comprising preparing solutions with varied concentrations of a surfactant and plotting values of surface tension measured at

every concentrations with SURFACE TENSIO METER A3  
manufactured by Kyowa Kagaku Co., Ltd., versus  
logarithms of the concentrations. The critical micelle  
concentration is the minimum concentration at which the  
5 surfactant can form micelle; the less the value thereof,  
the better surface activating property.

In the present invention, the content of a  
surfactant used in a lightsensitive material is  
preferably 0.01% by weight or more, and more preferably  
10 0.02% by weight or more of all the ingredients  
contained in a lightsensitive layer in which the  
surfactant is contained. The content of a surfactant  
in a lightsensitive material is preferably 5% by weight  
or less.

15 Only specific examples of surfactants that can be  
used in the present invention are presented below, but  
the invention, of course, is not limited to these them.

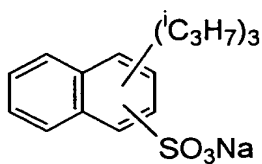
A-1



Critical micelle  
concentration  
(mol/L)

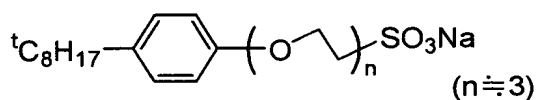
$$2.25 \times 10^{-3}$$

A-2



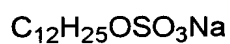
$3.65 \times 10^{-3}$

**A-3**



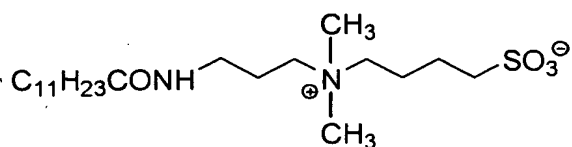
$$0.16 \times 10^{-3}$$

A-4



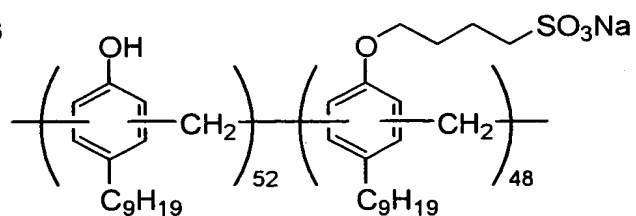
$$1.73 \times 10^{-3}$$

**A-5**



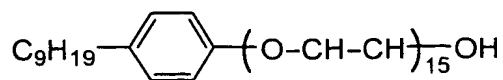
$$1.19 \times 10^{-3}$$

**A-6**



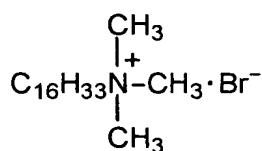
$$4.46 \times 10^{-6}$$

A-7



$0.12 \times 10^{-3}$

A-8



$1.0 \times 10^{-3}$

As a high boiling organic solvent that can be used in the present invention, a high boiling organic solvent having a dielectric constant of 7.0 or less is preferable. It can be selected from high boiling organic solvents having a boiling point of about 175°C or higher under atmospheric pressure such as phthalic esters, phosphoric esters, phosphonic esters, benzoic esters, esters of fatty acids, amides, phenols, alcohols, ethers, carboxylic acids, N,N-dialkylanilines, trialkylamines, hydrocarbons, oligomers and polymers. When two or more high boiling organic solvents are used after being mixed, if the mixture after mixing has a dielectric constant of 7.0 or less, it corresponds to the high boiling organic solvent.

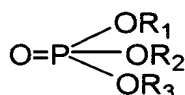
Further, such a high boiling organic solvent having a dielectric constant of 7.0 or less can be used after being mixed with a high boiling organic solvent having a dielectric constant of more than 7.0. In such a case, if the dielectric constant after mixing is 7.0 or less, the mixture corresponds to a high boiling organic solvent having a dielectric constant of 7.0 or less. The dielectric constant used herein refers to a specific inductive capacity with respect to vacuum, measured by a transformer bridge at a measuring temperature of 25°C, a measuring frequency of 10 kHz using a TRS-10T dielectric constant measuring device manufactured by Ando Electric Co., Ltd. The dielectric



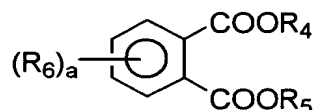
constant of organic solvents correlate to the square of the dipolar moment molecules of organic solvents and therefore represents the degree of the polarity of molecules. In general, a molecule with a high dielectric constant has a high polarity.

High boiling organic solvents preferably used in the present invention are high boiling organic solvents having a dielectric constant of 7.0 or less and represented by the following general formulas [S-1] to [S-8].

[S-1]



[S-2]



[S-3]



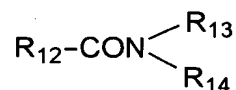
[S-4]



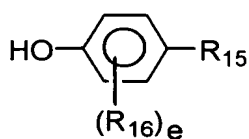
[S-5]



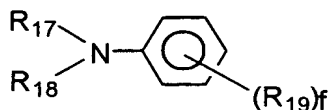
[S-6]



[S-7]



[S-8]



In formula [S-1], R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> each independently represent an aliphatic hydrocarbon group, an alicyclic hydrocarbon group or an aryl group. In formula [S-2], R<sub>4</sub> and R<sub>5</sub> each independently represent an aliphatic hydrocarbon group, an alicyclic hydrocarbon group or an aryl group, R<sub>6</sub> represents a halogen atom (F, Cl, Br, I;

the same below), an aliphatic hydrocarbon group, an aliphatic hydrocarbon oxy group, an aryloxy group, or an aliphatic hydrocarbon oxycarbonyl group, and a represents an integer of 0 to 3. When a is 2 or more, plural R<sub>6</sub>s may be the same or different.

In formula [S-3], Ar represents an aryl group, b represents an integer of 1 to 6, and R<sub>7</sub> represents a b-valent hydrocarbon group or a hydrocarbon groups bonded together through an ether bond. In formula [S-4], R<sub>8</sub> represents an aliphatic hydrocarbon group or an alicyclic hydrocarbon group, c represents an integer of 1 to 6, and R<sub>9</sub> represents a c-valent hydrocarbon group or hydrocarbon groups bonded together through an ether bond. In formula [S-5], d represents an integer of 2 to 6, R<sub>10</sub> represents a d-valent hydrocarbon group (except aromatic groups), and R<sub>11</sub> represents an aliphatic hydrocarbon group, an alicyclic hydrocarbon group or an aryl group. In formula [S-6], R<sub>12</sub>, R<sub>13</sub> and R<sub>14</sub> each independently represent an aliphatic hydrocarbon group, an alicyclic hydrocarbon group or an aryl group. R<sub>12</sub> and R<sub>13</sub>, or R<sub>13</sub> and R<sub>14</sub> may be bonded together to form a ring.

In formula [S-7], R<sub>15</sub> represents an aliphatic hydrocarbon group, an alicyclic hydrocarbon group, an aliphatic hydrocarbon oxycarbonyl group, an aliphatic hydrocarbon sulfonyl group, an arylsulfonyl group, an aryl group or a cyano group, R<sub>16</sub> represents a halogen

atom, an aliphatic hydrocarbon group, an alicyclic hydrocarbon group, an aryl group, an alkoxy group or an aryloxy group, and e represents an integer of 0 to 3. When e is 2 or more, plural R<sub>16</sub>s may be the same or different.

In formula [S-8], R<sub>17</sub> and R<sub>18</sub> each independently represent an aliphatic hydrocarbon group, an alicyclic hydrocarbon group or an aryl group, R<sub>19</sub> represents a halogen atom, an aliphatic hydrocarbon group, an alicyclic hydrocarbon group, an aryloxy group or an aliphatic hydrocarbon oxy group, and f represents an integer of 0 to 4. When f is 2 or more, plural R<sub>19</sub> may be the same or different. In formulas [S-1] to [S-8], when R<sub>1</sub> to R<sub>6</sub>, R<sub>8</sub> and R<sub>11</sub> to R<sub>19</sub> are aliphatic hydrocarbon groups or groups containing an aliphatic hydrocarbon group, an alkyl group may be either straight chain or branched, and may have an unsaturated bond and also may have a substituent. Examples of the substituent include a halogen atom, an aryl group, an alkoxy group, an aryloxy group, an alkoxycarbonyl group, a hydroxyl group, an acyloxy group and an epoxy group.

In formulas [S-1] to [S-8], when R<sub>1</sub> to R<sub>6</sub>, R<sub>8</sub> and R<sub>11</sub> to R<sub>19</sub> are alicyclic hydrocarbon groups or groups containing an alicyclic hydrocarbon group, each alicyclic hydrocarbon group may contain an unsaturated bond in its 3- to 8-membered ring, and may have a substituent or a cross-linking group. Examples of the

substituent include a halogen atom, a hydroxyl group, an acyl group, an aryl group, an alkoxy group, an epoxy group and an alkyl group. Examples of the cross-linking group include methylene, ethylene and isopropylidene.

In formulas [S-1] to [S-8], when R<sub>1</sub> to R<sub>6</sub>, R<sub>8</sub> and R<sub>11</sub> to R<sub>19</sub> are aryl groups or groups containing an aryl group, each aryl group may be substituted with a substituent such as a halogen atom, an alkyl group, an aryl group, an alkoxy group, an aryloxy group and an alkoxycarbonyl group.

In formulas [S-3], [S-4] and [S-5], when R<sub>7</sub>, R<sub>9</sub> or R<sub>10</sub> is a hydrocarbon group, the hydrocarbon group may contain a cyclic structure (e.g., a benzene ring, a cyclopentane ring and a cyclohexane ring) or an unsaturated bond, and also may have a substituent. Examples of the substituent include a halogen atom, a hydroxyl group, an acyloxy group, an aryl group, an alkoxy group, an aryloxy group and an epoxy group.

In formula [S-1], examples of R<sub>1</sub>, R<sub>2</sub> and R<sub>3</sub> include an aliphatic hydrocarbon group having a total number of carbon atoms of 1-24 (preferably 4-18), hereinafter, the total number of carbon atoms is referred to as C number, (e.g., n-butyl, 2-ethylhexyl, 3,3,5-trimethylhexyl, n-dodecyl, n-octadecyl, benzyl, 2-chloroethyl, 2,3-dichloropropyl, 2-butoxyethyl and 2-phenoxyethyl), an alicyclic hydrocarbon group of a C

number of 5-24 (preferably, 6-18) (e.g., cyclopentyl, cyclohexyl, 4-t-butylcyclohexyl and 4-methylcyclohexyl), or an aryl group having a C number of 6-24 (preferably 6-18) (e.g., phenyl, cresyl, p-nonylphenyl, xylyl,,  
5 cumenyl, p-methoxyphenyl and p-methoxycarbonylphenyl).

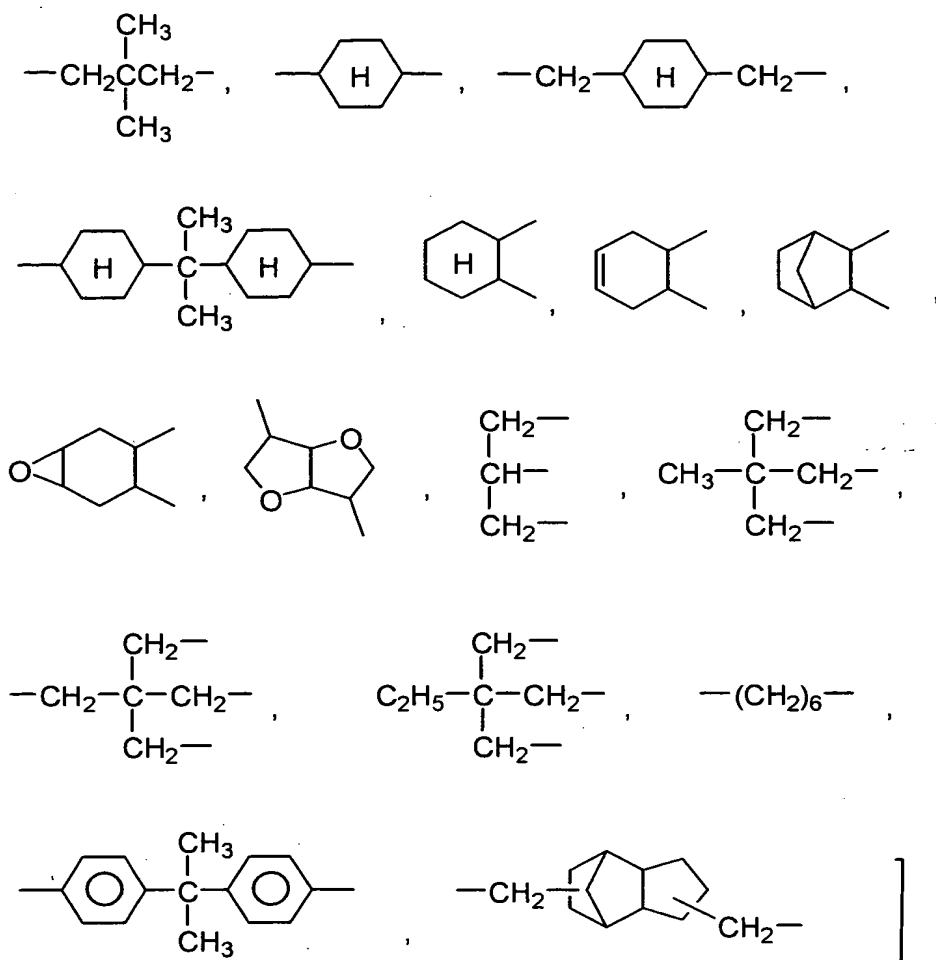
In formula [S-2], examples of  $R_4$  and  $R_5$  include an aliphatic hydrocarbon group having a C number of 1-24 (preferably, 4-18) (e.g., groups the same as the aliphatic hydrocarbon groups mentioned above for  $R_1$ ,  
10 ethoxycarbonylmethyl, 1,1-diethylpropyl, 2-ethyl-1-methylhexyl, cyclohexylmethyl and 1-ethyl-1,5-dimethylhexyl), an alicyclic hydrocarbon group having a C number of 5-24 (preferably, 6-18) (e.g., groups the same as the alicyclic hydrocarbon groups mentioned  
15 above for  $R_1$ , 3,3,5-trimethylcyclohexyl, menthyl, bornyl and 1-methylcyclohexyl), or an aryl group having a C number of 6-24 (preferably, 6-18) (e.g., the aryl groups mentioned above for  $R_1$ , 4-t-butylphenyl, 4-t-octylphenyl, 1,3,5-trimethylphenyl, 2,4-di-t-butylphenyl and 2,4-di-t-pentylphenyl); examples of  $R_6$   
20 include a halogen atom (preferably, Cl), an aliphatic hydrocarbon group having a C number of 1-18 (e.g., methyl, isopropyl, t-butyl and n-dodecyl), an aliphatic hydrocarbon oxy group having a C number of 1-18 (e.g., methoxy, n-butoxy, n-octyloxy, methoxyethoxy and  
25 benzyloxy), an aryloxy group having a C number of 6-18 (e.g., phenoxy, p-tolyloxy, 4-methoxyphenoxy and 4-t-

butylphenoxy), or an aliphatic hydrocarbon oxycarbonyl group having a C number of 2-19 (e.g., methoxycarbonyl, n-butoxycarbonyl and 2-ethylhexyloxycarbonyl); and a is 0 to 3 (preferably, 0 or 1).

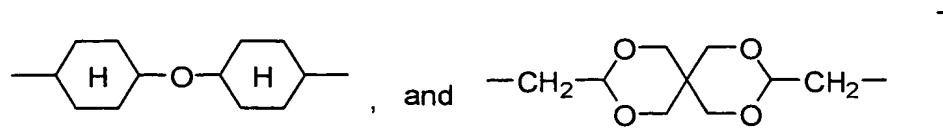
5        In formula [S-3], examples of Ar include an aryl group having a C number of 6-24 (preferably, 6-18)

(e.g., phenyl, 4-chlorophenyl, 4-methoxyphenyl, 1-naphthyl, 4-n-butoxyphenyl and 1,3,5-trimethylphenyl), b is an integer of 1 to 6 (preferably, 1 to 3),

10       examples of R<sub>7</sub> include a b-valent hydrocarbon group having a C number of 2-24 (preferably, 2-18) [e.g., the aliphatic hydrocarbon groups, alicyclic hydrocarbon groups, aryl groups, mentioned above for R<sub>4</sub>, -(CH<sub>2</sub>)<sub>2</sub>-,



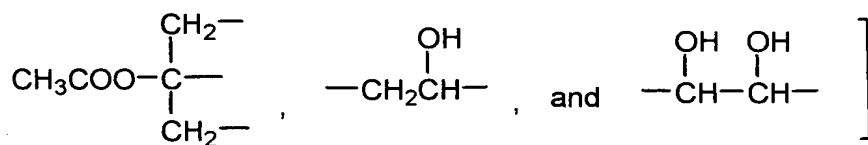
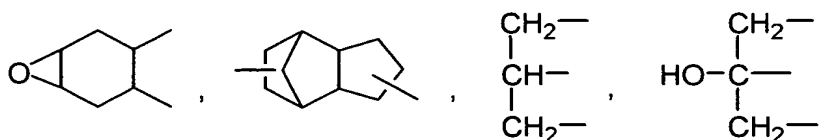
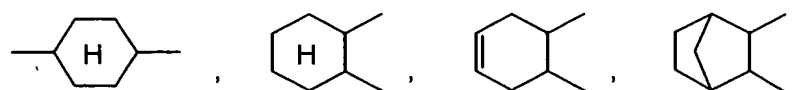
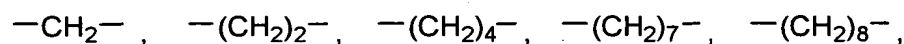
or c-valent hydrocarbon groups having a C number of 4-24 (preferably, 4-18) bonded together through an ether bond, [e.g.,  $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$ ,  $-\text{CH}_2\text{CH}_2(\text{OCH}_2\text{CH}_2)_3-$ ,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{CH}_2-$ ,



In formula [S-4], examples of  $R_8$  include an aliphatic hydrocarbon group having a C number of 1-24 (preferably, 1-17) (e.g., methyl, n-propyl, 1-hydroxyethyl, 1-ethylpentyl, n-undecyl, pentadecyl and

8,9-epoxyheptadecyl), or an alicyclic hydrocarbon group having a C number of 3-24 (preferably, 6-18) (e.g., cyclopropyl, cyclohexyl and 4-methylcyclohexyl), c is an integer of 1 to 6 (preferably, 1 to 3), examples of R<sub>9</sub> include a c-valent hydrocarbon group having a C number of 2-24 (preferably, 2-18) or a c-valent hydrocarbon group having a C number of 4-24 (preferably, 4-18) bonded together through an ether bond, (e.g., the groups presented for the aforementioned R<sub>7</sub>).

In formula [S-5], d is 2 to 6 (preferably, 2 or 3), examples of R<sub>10</sub> include a d-valent hydrocarbon group [e.g.,



examples of R<sub>11</sub> include an aliphatic hydrocarbon group having a C number of 1-24 (preferably, 4-18), an alicyclic hydrocarbon group having a C number of 5-24 (preferably, 6-18) or an aryl group having a C number of 6-24 (preferably, 6-18) (e.g., the alkyl, cycloalkyl



and aryl groups presented for the aforementioned  $R_4$ ).

In formula [S-6], examples of  $R_{12}$  include an aliphatic hydrocarbon group having a C number of 1-24 (preferably, 3-20) [e.g., n-propyl, 1-ethylpentyl, n-undecyl, n-pentadecyl, 2,4-di-t-pentylphenoxymethyl, 4-t-octylphenoxymethyl, 3-(2,4-di-t-butylphenoxy)propyl and 1-(2,4-di-t-butylphenoxy)propyl], an alicyclic hydrocarbon group having a C number of 5-24 (preferably, 6-18) (e.g., cyclohexyl and 4-methylcyclohexyl) or an aryl group having a C number of 6-24 (preferably, 6-18) (e.g., the aryl groups presented for the aforementioned Ar), examples of  $R_{13}$  and  $R_{14}$  include an aliphatic hydrocarbon group having a C number of 1-24 (preferably, 1-18) (e.g., methyl, ethyl, isopropyl, n-butyl, n-hexyl, 2-ethyl hexyl and n-dodecyl), an alicyclic hydrocarbon group having a C number of 5-18 (preferably, 6-15) (e.g., cyclopentyl and cyclopropyl) or an aryl group having a C number of 6-18 (preferably, 6-15) (e.g., phenyl, 1-naphthyl and p-tolyl).  $R_{13}$  and  $R_{14}$  may be bonded together to form together N a pyrrolidine ring, a piperidine ring or a morpholine ring.  $R_{12}$  and  $R_{13}$  may be bonded together to form a pyrrolidone ring.

In formula [S-7], examples of  $R_{15}$  include an aliphatic hydrocarbon group having a C number of 1-24 (preferably, 1-18) (e.g., methyl, isopropyl, t-butyl, t-pentyl, t-hexyl, t-octyl, 2-butyl, 2-hexyl, 2-octyl, 2-dodecyl, 2-hexadecyl and t-pentadecyl), an alicyclic

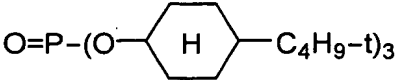
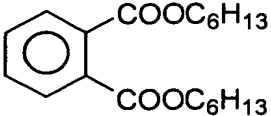
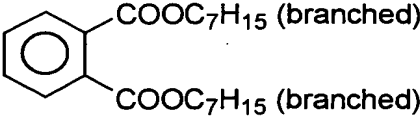
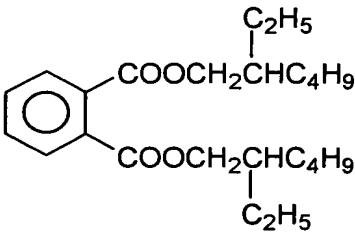
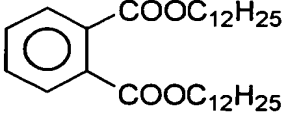
hydrocarbon group having a C number of 3-18 (preferably, 5-12) (e.g., cyclopentyl and cyclohexyl), an aliphatic hydrocarbon oxycarbonyl group having a C number of 2-24 (preferably, 5-17) (e.g., n-butoxycarbonyl, 2-ethylhexyloxycarbonyl and n-dodecyloxycarbonyl), an aliphatic hydrocarbon sulfonyl group having a C number of 1-24 (preferably, 1-18) (e.g., methylsulfonyl, n-butylsulfonyl and n-dodecylsulfonyl), an arylsulfonyl group having a C number of 6-30 (preferably, 6-24) (e.g., p-tolylsulfonyl, p-dodecylphenylsulfonyl, p-hexadecyloxyphenylsulfonyl), an aryl group having a C number of 6-32 (preferably, 6-24) (e.g., phenyl and p-tolyl) or a cyano group. Examples of  $R_{16}$  include a halogen atom (preferably, Cl), an aliphatic hydrocarbon group having a C number of 1-24 (preferably, 1-18) (e.g., the aliphatic hydrocarbon groups presented for the aforementioned  $R_{15}$ ), an alicyclic hydrocarbon group having a C number of 3-18 (preferably, 5-17) (e.g., cyclopentyl and cyclohexyl), an aryl group having a C number of 6-32 (preferably, 6-24) (e.g., phenyl and p-tolyl), an aliphatic hydrocarbon oxy group having a C number of 1-24 (preferably, 1-18) (e.g., methoxy, n-butoxy, 2-ethylhexyloxy, benzyloxy, n-dodecyloxy and n-hexadecyloxy), or an aryloxy group having a C number of 6-32 (preferably, 6-24) (e.g., phenoxy, p-t-butylphenoxy, p-t-octylphenoxy, m-pentadecylphenoxy and p-dodecyloxyphenoxy). e is an integer of 0 to 3

(preferably, 1 or 2).

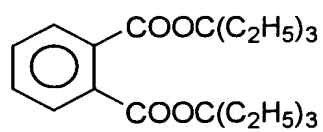
In formula [S-8],  $R_{17}$  and  $R_{18}$  are the same as the  
aforementioned  $R_{13}$  and  $R_{14}$ ,  $R_{19}$  is the same as the  
aforementioned  $R_{16}$ , and  $f$  is an integer of 0 to 4  
5 (preferably, 0 to 2).

Of the high boiling organic solvents represented  
by general formulas [S-1] to [S-8], the high boiling  
organic solvents represented by general formulas [S-1]  
(preferably,  $R_1$ ,  $R_2$  and  $R_3$  are each an alkyl group),  
10 [S-2], [S-3] (preferably,  $b$  is 1), [S-4], [S-5] and  
[S-7] are particularly preferable. The high boiling  
organic solvents represented by general formulas [S-1],  
[S-2], [S-4] and [S-5] are most preferable. Specific  
examples of the high boiling organic solvent to be used  
15 in the present invention will be presented below. The  
number indicated at the right side of each formula is  
dielectric constant thereof.

		dielectric constant
S-1	$\text{O}=\text{P}(\text{OC}_6\text{H}_{13})_3$	5.86
S-2	$\begin{array}{c} \text{O}=\text{P}(\text{OCH}_2\text{CHC}_4\text{H}_9)_3 \\   \\ \text{C}_2\text{H}_5 \end{array}$	4.80
S-3	$\begin{array}{c} \text{CH}_3 \\   \\ \text{O}=\text{P}(\text{OCH}_2\text{CH}_2\text{CHCH}_2\text{CCH}_2)_3 \\   \quad   \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	4.46
S-4	$\text{O}=\text{P}(\text{OC}_{12}\text{H}_{25})_3$	3.87
S-5	$\text{O}=\text{P}(\text{OC}_{16}\text{H}_{33})_3$	3.45
S-6	$\text{O}=\text{P}-(\text{O}(\text{CH}_2)_8\text{CH}=\text{CHC}_8\text{H}_{17})_3$	3.63

S-7		5.42
S-8		5.50
S-9		5.17
S-10		5.18
S-11		4.17

S-12



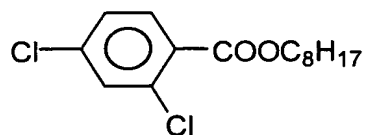
5.64

S-13



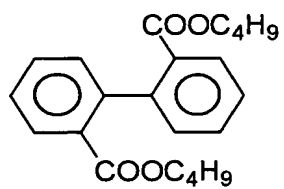
4.49

S-14



5.18

S-15



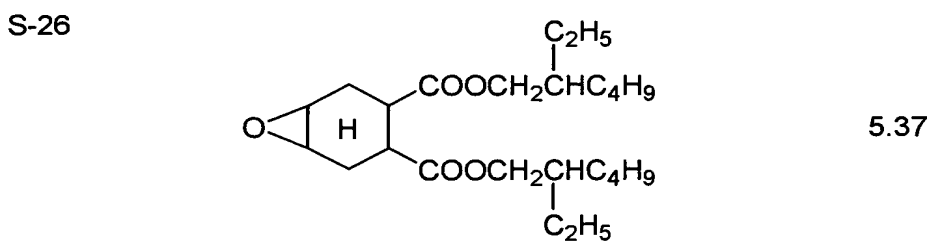
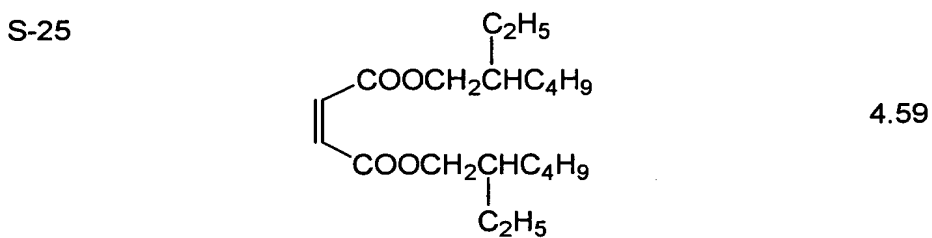
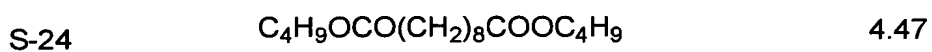
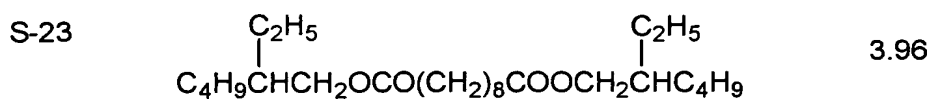
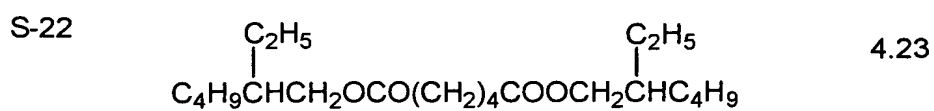
5.28

S-16



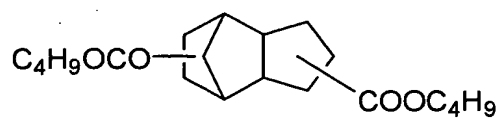
3.06

S-17	$\text{C}_8\text{H}_{17}\text{CH}(\text{O})\text{CH}(\text{CH}_2)_7\text{COOCH}_2\text{CH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9$	4.54
S-18	$\begin{array}{c} \text{OH} \qquad \qquad \text{CH}_3 \\   \qquad \qquad   \\ \text{CH}_3\text{CHCOOCH}_2\text{CH} \begin{cases} \text{CHCH}_2\text{C}_4\text{H}_9\text{-t} \\ \text{CH}_2\text{CH}_2\text{CHCH}_2\text{C}_4\text{H}_9\text{-t} \\ \qquad \qquad   \\ \qquad \qquad \text{CH}_2 \end{cases} \end{array}$	4.48
S-19	$\text{C}_4\text{H}_9\text{CH}(\text{C}_2\text{H}_5)\text{COOCH}_2\text{CH}_2\text{OCOCH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9$	4.26
S-20	$\text{C}_4\text{H}_9\text{CH}(\text{C}_2\text{H}_5)\text{COOCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{OCOCH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9$	3.54
S-21	$\text{C}_4\text{H}_9\text{CH}(\text{C}_2\text{H}_5)\text{COOCH}_2\text{---} \langle \text{H} \rangle \text{---} \text{CH}_2\text{OCOCH}(\text{C}_2\text{H}_5)\text{C}_4\text{H}_9$	3.87



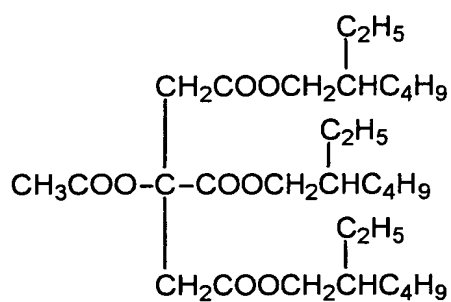


S-27



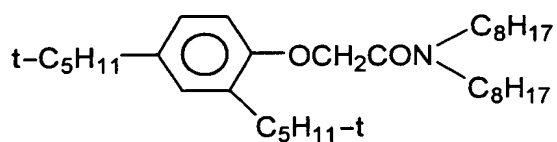
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S-28



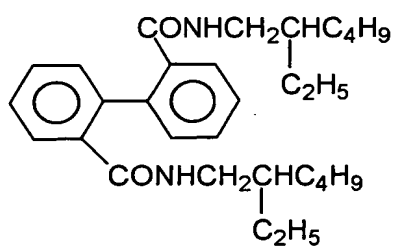
4.66

S-29



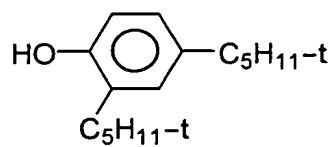
5.48

S-30



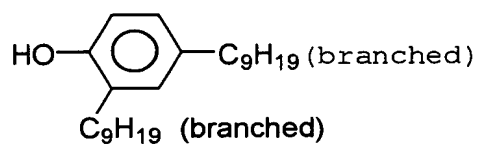
4.32

S-31



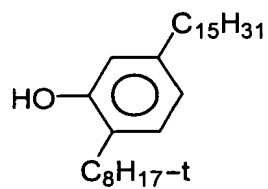
3.25

S-32



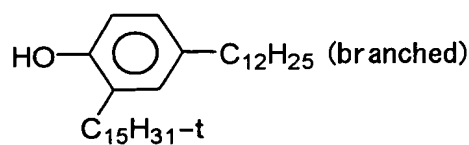
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S-33



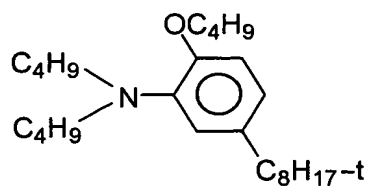
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S-34



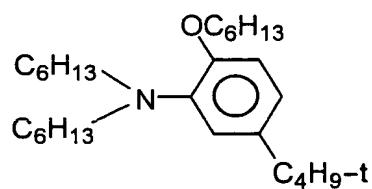
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S-35



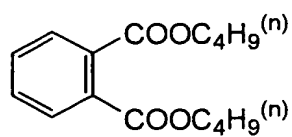
2.76

S-36



2.63

S-37



6.45

These high boiling organic solvents may be used individually or in combination of two or more of them [for example, a combination of di(2-ethylhexyl) phthalate and trioctyl phosphate, a combination of di(2-ethylhexyl) sebacate and triisononyl phosphate, and a combination of dibutyl phthalate and di(2-ethylhexyl) adipate]. When two or more high boiling organic solvents are used after being mixed, it is preferable that the dielectric constant after mixing is 7.0 or less.

Examples of compounds of high boiling organic solvents to be used in the present invention other than those mentioned above and/or methods for preparing these high boiling organic solvents will be described in U.S.P. Nos. 2,322,027, 2,533,514, 2,772,163, 2,835,579, 3,594,171, 3,676,137, 3,689,271, 3,700,454, 3,748,141, 3,764,336, 3,765,897, 3,912,515, 3,936,303, 4,004,929, 4,080,209, 4,127,413, 4,193,802, 4,207,393, 4,220,711, 4,239,851, 4,278,757, 4,353,979, 4,363,873, 4,430,421, 4,464,464, 4,483,918, 4,540,657, 4,684,606, 4,728,599 and 4,745,049, EP Nos. 276,319A, 286,253A, 289,820A, 309,158A, 309,159A and 309,160A, and JP-A's-48-47335, 50-26530, 51-25133, 51-26036, 51-277921, 51-27922, 51-149028, 52-46816, 53-1520, 53-1521, 53-15127, 53-146622, 54-106228, 56-64333, 56-81836, 59-204041, 61-84641, 62-118345, 62-247364, 63-167357, 63-214744, 63-301941, 64-68745, 1-101543 and 1-102454.

In the present invention, a high boiling organic solvent is preferably contained in the form of emulsion (fine dispersion). The average particle diameter of the emulsion is preferably 50  $\mu\text{m}$  or less, more preferably 10  $\mu\text{m}$  or less, particularly preferably 2  $\mu\text{m}$  or less, and most preferably 0.5  $\mu\text{m}$  or less. In preparation of the emulsion, it is possible to disperse by means only of mechanical stirring, but it is also preferable to use a surfactant. Further, it is also preferable to prepare the emulsion by adding a macromolecule such as gelatin thereto.

The content of a high boiling organic solvent in an emulsion, in % by weight (the weight of an organic solvent contained in 100 g of emulsion), is preferably 0.05% to 10%, more preferably 0.1% to 10%, and still more preferably 0.2% to 10%.

The general formula (IV) and general formula (V) will now be described in detail. In formula (IV), Q represents a N or P atom. Each of Ra1, Ra2, Ra3 and Ra4 preferably represents a substituted or unsubstituted alkyl having 1 to 20 carbon atoms (for example, methyl, butyl, hexyl, dodecyl, hydroxyethyl or trimethylammonioethyl, or an aryl substituted alkyl having 7 to 20 carbon atoms, such as benzyl, phenethyl or p-chlorobenzyl); a substituted or unsubstituted aryl having 6 to 20 carbon atoms (for example, phenyl or p-chlorophenyl); or a substituted or unsubstituted

heterocycle (for example, thienyl, furyl, pyrrolyl, imidazolyl or pyridyl). Provided, however, that two of Ra1, Ra2, Ra3 and Ra4 may be bonded with each other to thereby form a saturated ring (for example, pyrrolidine ring, piperidine ring, piperazine ring or morpholine ring); or three of Ra1, Ra2, Ra3 and Ra4 may cooperate with each other to thereby form an unsaturated ring (for example, pyridine ring, imidazole ring, quinoline ring or isoquinoline ring). Examples of substituted alkyls represented by Ra1, Ra2, Ra3 and Ra4 include those having a quaternary ammonium salt, a quaternary pyridinium salt or a quaternary phosphonium salt as a substituent.

Y represents an anion group, provided that Y does not exist in the event of an intramolecular salt. Y is, for example, a chloride ion, a bromide ion, an iodide ion, a nitrate ion, a sulfate ion, a p-toluenesulfonate ion or an oxalate ion.

Each of Ra5, Ra6 and Ra7 preferably represents a substituted or unsubstituted alkyl having 1 to 20 carbon atoms (for example, methyl, butyl, hexyl, dodecyl or hydroxyethyl, or an aryl substituted alkyl having 7 to 20 carbon atoms, such as benzyl, phenethyl or p-chlorobenzyl); a substituted or unsubstituted aryl having 6 to 20 carbon atoms (for example, phenyl or p-chlorophenyl); or a substituted or unsubstituted heterocycle (for example, thienyl, furyl, pyrrolyl,

imidazolyl or pyridyl). Provided, however, that two of Ra5, Ra6 and Ra7 may be bonded with each other to thereby form a saturated ring (for example, pyrrolidine ring, piperidine ring, piperazine ring or morpholine ring); or Ra5, Ra6 and Ra7 may cooperate with each other to thereby form an unsaturated ring (for example, pyridine ring, imidazole ring, quinoline ring or isoquinoline ring).

Ra8 represents a group constituted by each or any combination of alkylene, arylene, -O-, -S- and -CO<sub>2</sub>-, provided that each of -O-, -S- and -CO<sub>2</sub>- is bonded so as to be adjacent to alkylene or arylene. The alkylene may be substituted with, for example, a hydroxyl group as a substituent. The alkylene preferably has 1 to 10 carbon atoms, and can be any of, for example, trimethylene, pentamethylene, heptamethylene, nonamethylene, -CH<sub>2</sub>CH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>-, -(CH<sub>2</sub>CH<sub>2</sub>O)<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>-, -(CH<sub>2</sub>CH<sub>2</sub>O)<sub>3</sub>-CH<sub>2</sub>CH<sub>2</sub>-, -(CH<sub>2</sub>CH<sub>2</sub>S)<sub>3</sub>-CH<sub>2</sub>CH<sub>2</sub>- and -CH<sub>2</sub>CH<sub>2</sub>COOCH<sub>2</sub>CH<sub>2</sub>OCOCH<sub>2</sub>CH<sub>2</sub>-.

Ra9, Ra10 and Ra11 have the same meaning as Ra5, Ra6 and Ra7.

The compound of general formula (IV) according to the present invention is preferably the compound of general formula (V).

The compound of general formula (IV) or general formula (V) according to the present invention is preferably dissolved in a water-soluble solvent such as

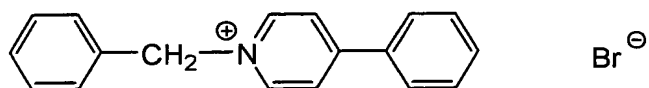
any of water, methanol and ethanol or a mixed solvent thereof before the addition to the emulsion.

5 The timing of addition of the compound of general formula (IV) or general formula (V) according to the present invention may be before or after the addition of the sensitizing dye. Preferred addition amounts thereof are such that the compound is contained in the silver halide emulsion in an amount of 1 to 50 mol%, more preferably 2 to 25 mol%, based on the sensitizing dye. These addition amounts are preferred from the viewpoint that, when the addition amount of the compound of general formula (IV) or general formula (V) for use in the present invention is greater than the above, the amount of sensitizing dye which can be adsorbed on emulsion grains is occasionally unfavorably reduced.

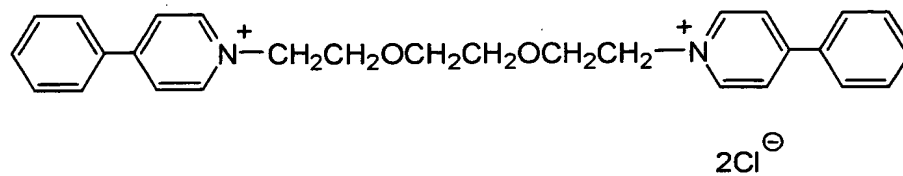
10 The compound of general formula (IV) or general formula (V) according to the present invention can be easily synthesized by the same synthetic process as described in Quart. Rev., 16, 163 (1962).

20 Representative examples of the compounds of general formula (IV) and general formula (V) which can be used in the present invention will be set forth below, to which, however, the present invention is in no way limited.

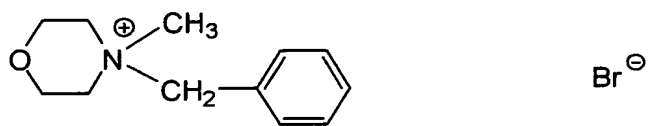
IV-1



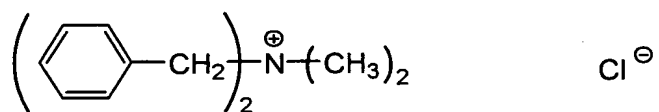
IV-2



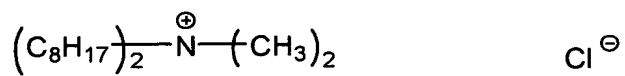
IV-3



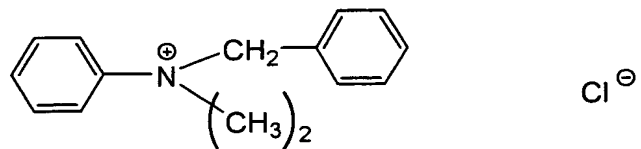
IV-4



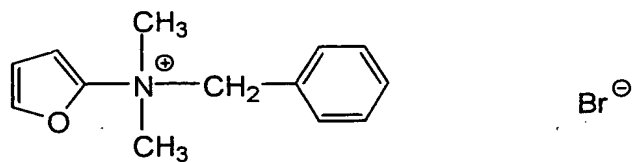
IV-5



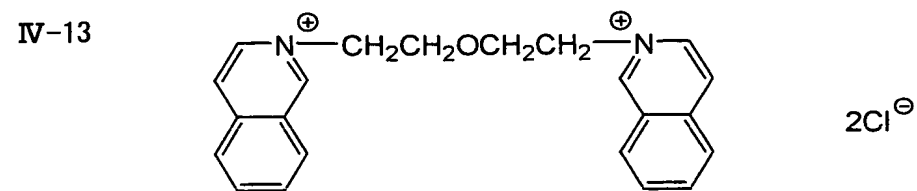
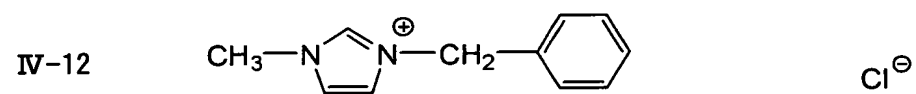
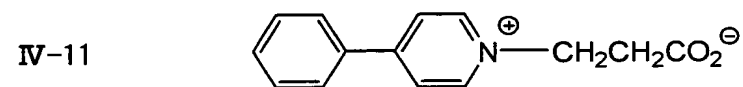
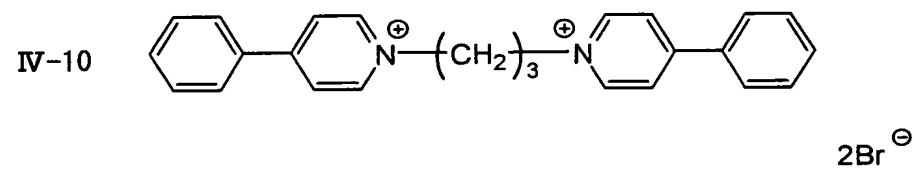
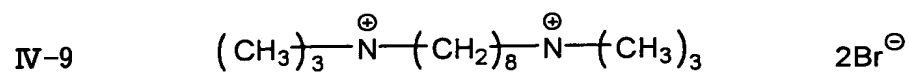
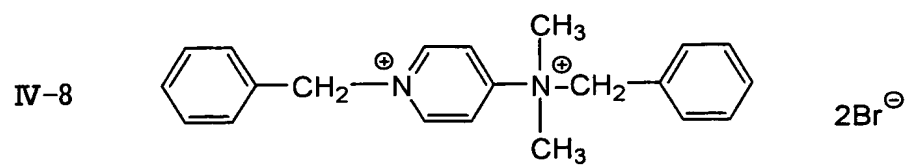
IV-6

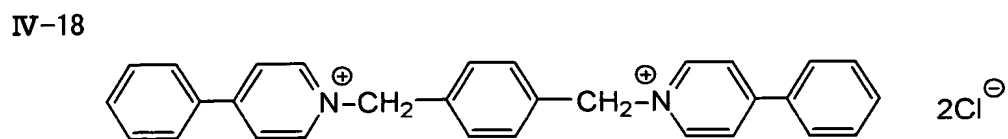
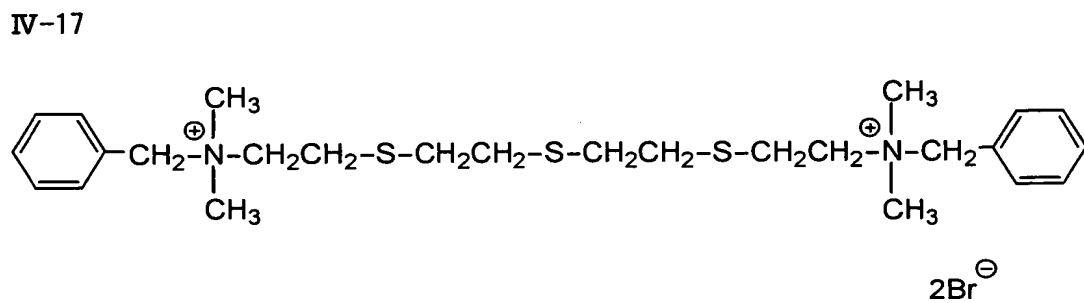
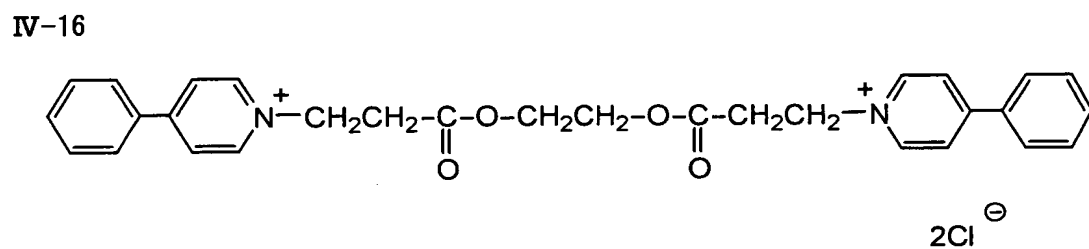
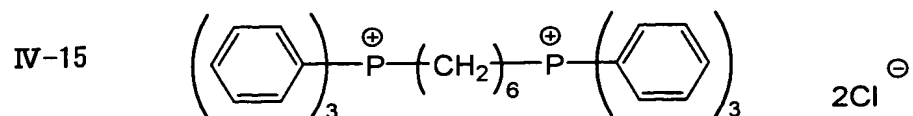
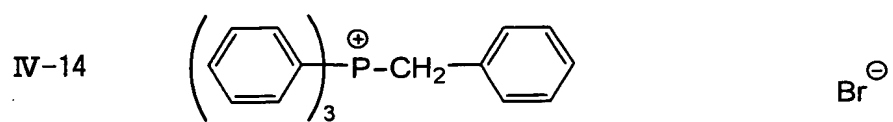


IV-7









Next, general formulas (VI) to (XI) will be described in detail.

All of the compounds represented by formulas (VI) to (XI) are reducing compounds. The oxidation potential of the compounds may be measured by the methods described in "DENKIKAGAKUSOKUTEIHO (Electrochemistry Measuring Method)" (Akira Shimazaki, pp.150-208, Gihodo Publisher), and "JIKKENKAGAKUKOUZA (NIHONKAGAKUKAI ed., 4th edition, vol.9, pp.282-344, MARUZEN). For example, the measurement can be made by a rotary disk voltammetry technique. Specifically, a sample is dissolved in a solution of methanol : Briton-Robinson buffer (pH6.5) = 10%: 90% (volume ratio). After nitrogen gas is made to pass through the sample for 10 min, the measurement can be made using a rotary disk electrode made of glassy carbon (RDE), a platinum wire, and a saturated calomel electrode, as working electrode, counter electrode and reference electrode, respectively, at 25°C, 1000rpm, and 20mV/sec sweep speed. From voltammogram obtained, half-wave potential ( $E_{1/2}$ ) can be obtained.

The reducing compounds used in the invention has an oxidation potential preferably in a range of about -0.3V to about 1.0V, more preferably in a range of about -0.1V to about 0.8V, and especially preferably in a range of about 0 to about 0.6V.

In general formula (VI), examples of the alkyl,

alkenyl group and the alkynyl group represented by Rb1 and Rb2 include a substituted or unsubstituted, straight chain or branched alkyl group having 1-10 carbon atoms (e.g., methyl, ethyl, isopropyl, n-propyl, n-butyl, t-butyl, 2-pentyl, n-hexyl, n-octyl, t-octyl, 2-ethylhexyl, hydroxymethyl, 2-hydroxyethyl, 1-hydroxyethyl, diethylaminoethyl, dibutylaminoethyl, n-butoxypropyl and methoxymethyl), a substituted or unsubstituted cyclic alkyl group having 3-6 carbon atoms (e.g., cyclopropyl, cyclopentyl and cyclohexyl), an alkenyl group having 2-10 carbon atoms (e.g., allyl, 2-butenyl, 3-pentenyl and 2-cyclohexenyl), an alkynyl group having 2-10 carbon atoms (e.g., propargyl and 3-pentynyl), and an aralkyl group having 7-12 carbon atoms (e.g., benzyl). Examples of the aryl group include a substituted or unsubstituted phenyl group having 6-12 carbon atoms (e.g., unsubstituted phenyl and 4-methylphenyl).

In general formula (VI), examples of the alkyl group, the alkenyl group and the alkynyl group represented by Rb3 and Rb4 include a substituted or unsubstituted, straight chain or branched alkyl group having 1-10 carbon atoms (e.g., methyl, ethyl, isopropyl, n-propyl, n-butyl, t-butyl, 2-pentyl, n-hexyl, n-octyl, t-octyl, 2-ethylhexyl, 2-hydroxyethyl, diethylaminoethyl, dibutylaminoethyl, methoxyethyl and ethoxyethoxyethyl), a substituted or unsubstituted

cyclic alkyl group having 3-6 carbon atoms (e.g., cyclopropyl, cyclopentyl and cyclohexyl), an alkenyl group having 2-10 carbon atoms (e.g., allyl, 2-butenyl, 3-pentenyl and 2-cyclohexenyl), an alkynyl group having  
5 2-10 carbon atoms (e.g., propargyl and 3-pentynyl), and an aralkyl group having 7-12 carbon atoms (e.g., benzyl). Examples of the aryl group include a substituted or unsubstituted phenyl group having 6-12 carbon atoms (e.g., unsubstituted phenyl and 4-  
10 methylphenyl) and a substituted or unsubstituted naphthyl group having 10-16 carbon atoms (e.g., unsubstituted naphthyl).

Rb1 or Rb2 and Rb3 or Rb4 may be bonded together to form a ring.

15 In general formula (VI), examples of the alkyl group, the alkenyl group and the alkynyl group represented by Rb5 include a substituted or unsubstituted, straight chain or branched alkyl group having 1-8 carbon atoms (e.g., methyl, ethyl, isopropyl, n-propyl, n-butyl, t-butyl, 2-pentyl, n-hexyl, n-octyl, 20 t-octyl, 2-ethylhexyl, 2-hydroxyethyl and diethylaminoethyl), a substituted or unsubstituted cyclic alkyl group having 3-6 carbon atoms (e.g., cyclopropyl, cyclopentyl and cyclohexyl), an alkenyl  
25 group having 2-10 carbon atoms (e.g., allyl, 2-butenyl and 3-pentenyl), an alkynyl group having 2-10 carbon atoms (e.g., propargyl and 3-pentynyl), and an aralkyl

group having 7-12 carbon atoms (e.g., benzyl).

Examples of the aryl group include a substituted or unsubstituted phenyl group having 6-16 carbon atoms (e.g., unsubstituted phenyl, 4-methylphenyl, 4-(2-

5 hydroxyethyl)-phenyl, 4-sulfophenyl, 4-chlorophenyl, 4-trifluoromethylphenyl, 3-trifluoromethylphenyl, 4-carboxyphenyl, 2,5-dimethylphenyl, 4-dimethylaminophenyl, 4-(3-carboxypropionylamino)-phenyl, 4-methoxyphenyl, 2-methoxyphenyl, 2,5-dimethoxyphenyl  
10 and 2,4,6-trimethylphenyl) and a substituted or unsubstituted naphthyl group having 10-16 carbon atoms (e.g., unsubstituted naphthyl and 4-methylnaphthyl).

Examples of the heterocyclic group include pyridyl, furyl, imidazolyl, piperidyl and morpholyl.

15 Further, Rb1, Rb2, Rb3, Rb4 and Rb5 may further be substituted with the substituents of Yy set forth below. Examples of the substituent Yy include a halogen atom (e.g., a fluorine atom, chlorine atom, and bromine atom), an alkyl group (e.g., methyl, ethyl,  
20 isopropyl, n-propyl, t-butyl), an alkenyl group (e.g., allyl, and 2-butenyl), an alkynyl group (e.g., propargyl), an aralkyl group (e.g., benzyl), an aryl group (e.g., phenyl, naphthyl, and 4-methylphenyl), a heterocyclic group (e.g., pyridyl, furyl, imidazolyl,  
25 piperidyl, and morpholino), an alkoxy group (e.g., methoxy, ethoxy, butoxy, 2-ethylhexyloxy, ethoxyethoxy, and methoxyethoxy), an aryloxy group (e.g., phenoxy and

2-naphthyloxy), an amino group (e.g., unsubstituted amino, dimethylamino, diethylamino, dipropylamino, dibutylamino, ethylamino, and anilino), an acylamino group (e.g., acetylamino and benzoylamino), an ureido group (e.g., unsubstituted ureido, and N-methylureido),  
5 an urethane group (e.g., methoxycarbonylamino and phenoxy carbonylamino), a sulfonylamino group (e.g., methylsulfonylamino and phenylsulfonylamino), a sulfamoyl group (e.g., unsubstituted sulfamoyl, N,N-dimethylsulfamoyl and N-phenylsulfamoyl), a carbamoyl group (e.g., unsubstituted carbamoyl,  
10 N,N-diethylcarbamoyl, and N-phenylcarbamoyl), a sulfonyl group (e.g., mesyl and tosyl), a sulfinyl group (e.g., methylsulfinyl and phenylsulfinyl),  
15 an alkyloxycarbonyl group (e.g., methoxycarbonyl and ethoxycarbonyl), an aryloxycarbonyl group (e.g., phenoxy carbonyl), an acyl group (e.g., acetyl, benzoyl, formyl, and pivaloyl), an acyloxy group (e.g., acetoxy and benzoyloxy), an amide phosphate group (e.g.,  
20 N,N-diethyl amide phosphate), a cyano group, a sulfo group, thiosulfonic acid group, a sulfinic acid, a carboxy group, a hydroxy group, a phosphono group, a nitro group, an ammonio group, a phosphonio group, a hydrazino group and thiazolino group. These groups can  
25 be further substituted. If two or more substituents exist, these substituents can be the same or different.

It is preferable that in general formula (VI), Rb1

and Rb2 each independently are a substituted or unsubstituted, straight chain or branched alkyl group having 1-4 carbon atoms or a substituted or unsubstituted phenyl group having 6-10 carbon atoms,

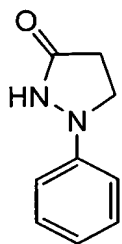
5 Rb3 and Rb4 each independently are a hydrogen atom, a substituted or unsubstituted, straight chain or branched alkyl group having 1-4 carbon atoms or a substituted or unsubstituted phenyl group having 6-10 carbon atoms, Rb5 is a substituted or unsubstituted  
10 phenyl group having 6-12 carbon atoms, and the compound represented by general formula (VI) has a molecular weight of 350 or less.

Further, it is preferable that in general formula (VI), Rb1 and Rb2 each are a substituted or  
15 unsubstituted straight chain alkyl group having 1-3 carbon atoms, Rb3 and Rb4 each are a hydrogen atom, Rb5 is a substituted or unsubstituted phenyl group having 6-10 carbon atoms, and the compound represented by general formula (VI) has a molecular weight of 300 or  
20 less. Furthermore, it is most preferable that in general formula (VI), the sum of the numbers of carbon atoms of Rb1 through Rb5 is 11 or less.

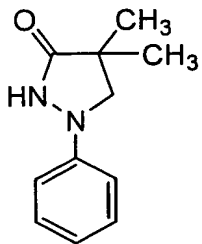
The following are specific examples of the compound represented by general formula (VI), but the  
25 present invention is not restricted to them.



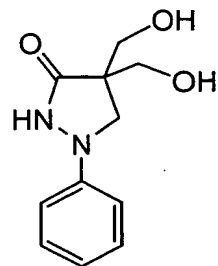
(VI-1)



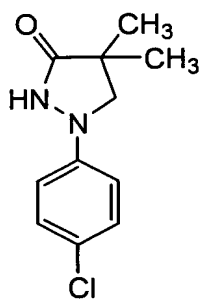
(VI-2)



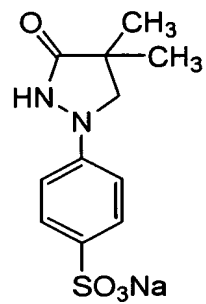
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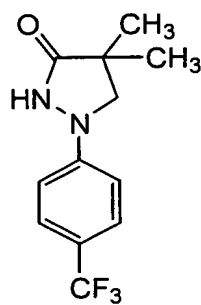
(VI-4)



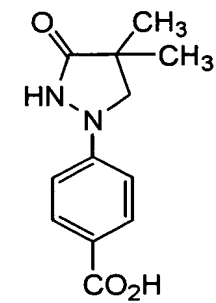
(VI-5)



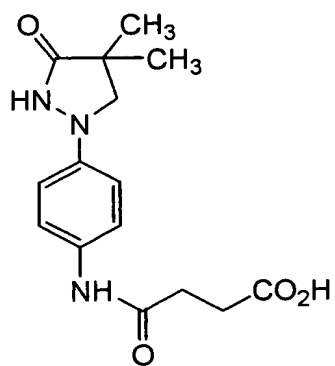
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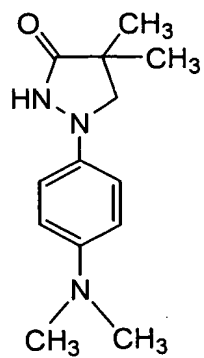
(VI-7)



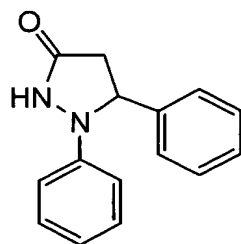
(VI-8)



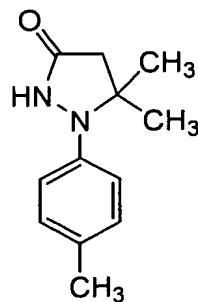
(VI-9)



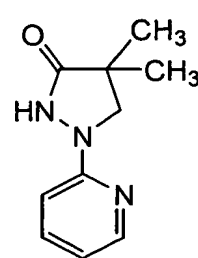
(VI-10)



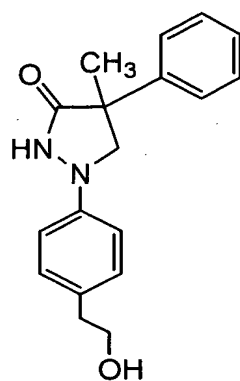
(VI-11)



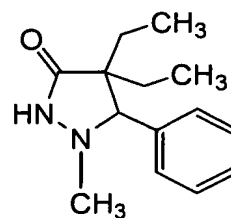
(VI-12)



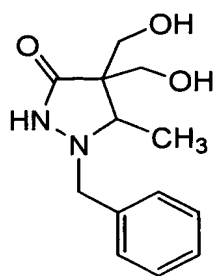
(VI-13)



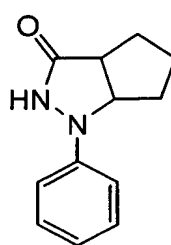
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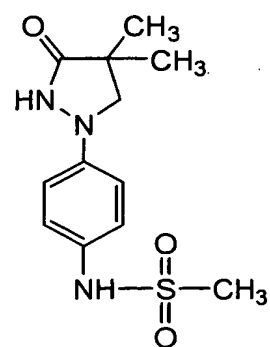
(VI-15)



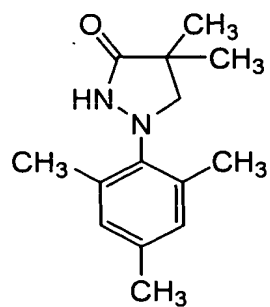
(VI-16)



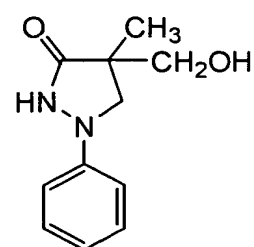
(VI-17)



(VI-18)



(VI-19)



The compounds represented by general formula (VI) are readily available as chemicals on the market or as compounds synthesized from these chemicals on the market by known methods. The compounds of general  
5 formula (VI) can be easily prepared by the synthesis methods described, for example, in Journal of Chemical Society (J. Chem. Soc.,) 408 (1954), U.S.P. Nos. 2,743,279 (1953) and 2,772,282 (1953), and methods according to those methods.

10 The compound represented by general formula (VI) is preferably added to a layer adjacent to an emulsion layer or another layer before or during application of a coating solution, thereby being added to the emulsion layer through its dispersion therein. It is also  
15 possible to add that compound before, during or after completion of the chemical sensitization in preparation of an emulsion. The compound represented by general formula (VI) can be added to either a photosensitive layer or a non-photosensitive layer.

20 The preferable addition amount of that compound depends greatly on the manner of its addition as described above and the kind of the compound to be added, but in general, the compound is used in an amount of from  $5 \times 10^{-6}$  mol to 0.05 mol, preferably  
25 from  $1 \times 10^{-5}$  mol to 0.005 mol, per mol of an lightsensitive silver halide. The addition of the compound in an amount more than the amount mentioned

above is not preferable because it will result in some adverse effect such as increase of fogging.

It is preferable that a compound represented by general formula (VI) is added after being dissolved in a water-soluble solvent. The pH of the solution may be decreased or increased with an acid or a base, and a surfactant may exist together with that compound. Further, that compound may be added after being formed into an emulsified dispersion and then being dissolved in a high boiling organic solvent. Alternatively, it may be added after being formed into a fine crystal dispersion by a known dispersing process.

The compound represented by general formula (VII) will be described in more detail. First, a hydrazine structure represented by  $Rb_6Rb_7N-NRb_8Rb_9$ , which is preferably used as Hy, will be described in detail.

$Rb_6$ ,  $Rb_7$ ,  $Rb_8$  and  $Rb_9$  each represent an alkyl group, an alkenyl group, an alkynyl group, an aryl group or a heterocyclic group. Each of the combinations of  $Rb_6$  and  $Rb_7$ ,  $Rb_8$  and  $Rb_9$ ,  $Rb_6$  and  $Rb_8$ , and  $Rb_7$  and  $Rb_9$  may be bonded together to form a ring, but no aromatic heterocycle (ex. pyridazine, and pyrazole) is formed, provided that at least one of  $Rb_6$ ,  $Rb_7$ ,  $Rb_8$  and  $Rb_9$  is an alkylene group, an alkenylene group, an alkynylene group, an arylene group or a bivalent heterocyclic moiety for being substituted with  $-(M)_{k2}-(Het)_{k1}$  in the general formula (VII).

Examples of Rb6, Rb7, Rb8 and Rb9 include an unsubstituted alkyl, alkenyl and alkynyl groups having 1-18 carbon atoms (preferably, 1-8 carbon atoms) (e.g., a methyl group, an ethyl group, a propyl group, an isopropyl group, a butyl group, an isobutyl group, a hexyl group, an octyl group, a dodecyl group, an octadecyl group, a cyclopentyl group, a cyclopropyl group and a cyclohexyl group), a substituted alkyl, alkenyl and alkynyl groups having 1-18 carbon atoms (preferably, 1-8 carbon atoms).

Each of the combinations Rb6 and Rb7, Rb8 and Rb9, Rb6 and Rb8, and Rb7 and Rb9 may be bonded together to form a ring, but no aromatic heterocycle is formed. These rings may be substituted with the aforementioned substituent Yy.

More preferable examples of Rb6, Rb7, Rb8 and Rb9 include an unsubstituted alkyl, alkenyl and alkynyl groups and a substituted alkyl, alkenyl and alkynyl groups. It is also preferable for Rb6, Rb7, Rb8 and Rb9 that each of the combinations Rb6 and Rb7, Rb8 and Rb9, Rb6 and Rb8, and Rb7 and Rb9 is bonded together to form an alkylene group containing no atom other than carbon atoms (e.g., an oxygen atom, a sulfur atom and a nitrogen atom) as atoms constituting a ring, wherein the alkylene group may have a substituent (for example, the aforementioned substituent Yy).

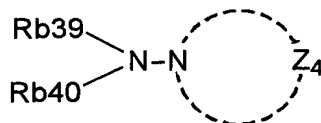
More preferably, each of the carbon atom of Rb6,

Rb7, Rb8 and Rb9 which directly attaches to a nitrogen atom of the hydrazine form an unsubstituted methylene group. Particularly preferable examples of Rb6, Rb7, Rb8 and Rb9 include an unsubstituted alkyl group having 1-6 carbon atoms (e.g., methyl, ethyl, propyl and butyl), a substituted alkyl group having 1-8 carbon atoms {for example, a sulfoalkyl group (e.g., 2-sulfoethyl, 3-sulfopropyl, 4-sulfobutyl and 3-sulfobutyl), a carboxyalkyl group (e.g., carboxymethyl and 2-carboxyethyl), and a hydroxyalkyl group (e.g., 2-hydroxyethyl)}. It is also preferable for Rb6, Rb7, Rb8 and Rb9 that each of the combinations Rb6 and Rb7, Rb8 and Rb9, Rb6 and Rb8, and Rb7 and Rb9 is combined through an alkylene chain to form a 5-, 6- or 7-membered ring.

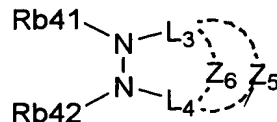
The hydrazine group represented by Rb6Rb7N-NRb8Rb9 is substituted with at least one -(M)<sub>k2</sub>-(Het)<sub>k1</sub> the substitution site of which may be any of Rb6, Rb7, Rb8 and Rb9.

Further, it is particularly preferable that the compound represented by Rb6Rb7N-NRb8Rb9, which is used in the present invention, is a compound selected from the following general formulas (Hy-1), (Hy-2) and (Hy-3).

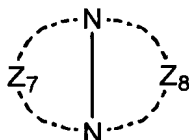
(Hy-1)



(Hy-2)



(Hy-3)



In the formulas, Rb39, Rb40, Rb41 and Rb42 each independently represent an alkyl group, an alkenyl group, an alkynyl group, an aryl group or a heterocyclic group. Each of the combinations Rb39 and Rb40, and Rb41 and Rb42 may be bonded together to form a ring.

Z<sub>4</sub> represents an alkylene group having 4, 5 or 6 carbon atoms. Z<sub>5</sub> represents an alkylene group having 2 carbon atoms. Z<sub>6</sub> represents an alkylene group having 1 or 2 carbon atoms. Z<sub>7</sub> and Z<sub>8</sub> each represent an alkylene group having 3 carbon atoms. L<sub>3</sub> and L<sub>4</sub> each represent a methine group.

Each of general formulas (Hy-1), (Hy-2) and (Hy-3) is substituted with at least one -(M)<sub>k2</sub>-(Het)<sub>k1</sub>. A compound selected from general formulas (Hy-1) and (Hy-2) is more preferable. A compound selected from general formula (Hy-1) is particularly preferable.

General formula (Hy-1) will be described in detail below. Rb39 and Rb40 have the same meaning as Rb6, Rb7,

Rb8 and Rb9, and their preferable ranges are also the same as those of Rb6, Rb7, Rb8 and Rb9. Particularly preferable case is that an alkyl group, Rb39 and Rb40 are bonded together to form an unsubstituted tetramethylene group or a pentamethylene group.

Z<sub>4</sub> represents an alkylene group having 4, 5 or 6 carbon atoms, and a preferable case is that Z<sub>4</sub> is an alkylene group having 4 or 5 carbon atoms, provided that no oxo group is bonded to a carbon atom directly attached to a nitrogen atom of the hydrazine. The alkylene group may be either unsubstituted or substituted. Examples of the substituent include the aforementioned substituent Yy and it is preferable that a carbon atom directly bonded to a nitrogen atom of the hydrazine forms an unsubstituted methylene group. Z<sub>4</sub> is particularly preferably an unsubstituted tetramethylene group or an unsubstituted pentamethylene group. The hydrazine group represented by general formula (Hy-1) is substituted with at least one -(M)<sup>k2</sup>-(Het)<sup>k1</sup> the substitution site of which may be any of Rb39, Rb40 and Z<sub>4</sub>, and preferably is Rb39 and Rb40.

General formula (Hy-2) will be described in detail below. Rb41 and Rb42 have the same meaning as Rb6, Rb7, Rb8 and Rb9, and their preferable ranges are also the same as those of Rb6, Rb7, Rb8 and Rb9. Particularly preferable case is that an alkyl group, Rb41 and Rb42 are bonded together to form a trimethylene group. Z<sub>5</sub>



represents an alkylene group having 2 carbon atoms. Z<sub>6</sub> represents an alkylene group having 1 or 2 carbon atoms. These alkylene groups may be either unsubstituted or substituted. Examples of the substituent include the  
5      aforementioned substituent Yy. More preferable as Z<sub>5</sub> is an unsubstituted ethylene group. More preferable as Z<sub>6</sub> is an unsubstituted methylene group and an ethylene group. L<sub>3</sub> and L<sub>4</sub> each represent substituted and unsubstituted methine groups. Examples of the  
10      substituent include the aforementioned substituent Yy. The substituent is preferably an unsubstituted alkyl group (e.g., a methyl group and a t-butyl group). More preferably L<sub>3</sub> and L<sub>4</sub> each represent an unsubstituted methine group. The hydrazine group represented by  
15      general formula (Hy-2) is substituted with at least one - (M)<sub>k2</sub> - (Het)<sub>k1</sub> the substitution site of which may be any of Rb<sub>41</sub>, Rb<sub>42</sub>, Z<sub>5</sub>, Z<sub>6</sub>, L<sub>3</sub> and L<sub>4</sub>, and preferably is Rb<sub>41</sub> and Rb<sub>42</sub>.

General formula (Hy-3) will be described in detail  
20      below. Z<sub>7</sub> and Z<sub>8</sub> each independently represent an alkylene group having 3 carbon atoms, provided that no oxo group is substituted for a carbon atom directly bonded to a nitrogen atom of the hydrazine. The alkylene group may be either unsubstituted or  
25      substituted. Examples of the substituent include the aforementioned substituent Yy and it is preferable that a carbon atom directly bonded to a nitrogen atom of the

hydrazine forms an unsubstituted methylene group. Z<sub>7</sub> and Z<sub>8</sub> are particularly preferably an unsubstituted trimethylene group, a trimethylene group substituted with unsubstituted alkyl group (e.g., 2,2-

5 dimethyltrimethylene). The hydrazine group represented by general formula (Hy-3) is substituted with at least one -(M)<sup>k2</sup>-(Het)<sup>k1</sup> the substitution site of which may be any of Z<sub>7</sub> and Z<sub>8</sub>.

In general formula (NII), the group represented by  
10 Het preferably has any of the following structures (1)-(5):

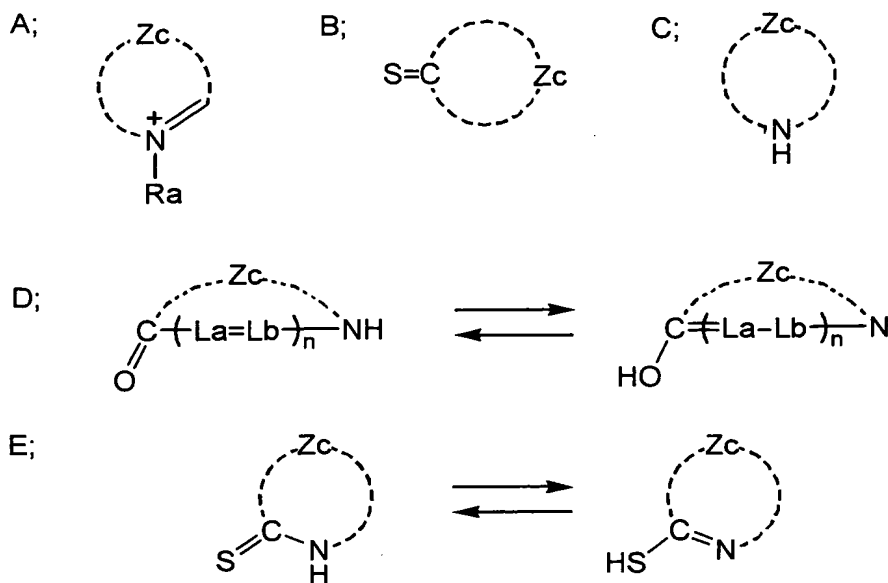
(1) A 5-, 6- or 7-membered heterocycle having two or more hetero atoms.

(2) A 5-, 6- or 7-membered, nitrogen-containing  
15 heterocycle having a quaternary nitrogen atom represented by the following A.

(3) A 5-, 6- or 7-membered, nitrogen-containing heterocycle having a thioxo group represented by the following B.

20 (4) A 5-, 6- or 7-membered, nitrogen-containing heterocycle represented by the following C.

(5) A 5-, 6- or 7-membered, nitrogen-containing heterocycle represented by the following D and E.



Zc represents a group of atoms required to form a 5-, 6-, or 7-membered nitrogen-containing heterocycle.  
 Ra represents an aliphatic group.  
 La and Lb each represent a methyne group.  
 n represents 0, 1 or 2.

Examples of Ra include those presented as examples of the alkyl group, the alkenyl group, and the alkynyl group for Rb6, Rb7, Rb8 and Rb9.

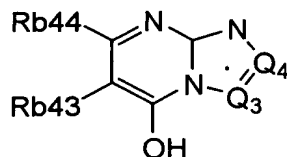
A nitrogen-containing heterocycle containing Zc as a ring-constituting atom is a 5-, 6- or 7-membered heterocycle that contains at least one nitrogen atom and may also contain a hetero atom other than the nitrogen atom (e.g., an oxygen atom, a sulfur atom, a selenium atom and tellurium atom), and preferably is an azole ring (e.g., imidazole, triazole, tetrazole, oxazole, thiazole, selenazole, benzimidazole, benzotriazole, benzoxazole, benzothiazole, thiadiazole, oxadiazole, benzoselenazole, pyrazole, naphthothiazole, naphthoimidazole, naphthoxazole, azabenzimidazole and purine), a pyrimidine ring, a triazine ring and an

azaindene ring (e.g., triazaindene, tetrazaindene and pentazaindene).

It is to be noted that a group represented by Het is substituted with at least one  $-(M)k_2-(Hy)$ .

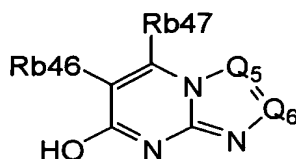
- 5 More preferred as Het are the compounds represented by the following general formulas (Het-a), (Het-b), (Het-c), (Het-d) and (Het-e).

(Het-a)



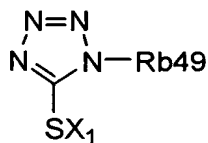
$Q_3=N$ ,  $Q_4=C-Rb45$  or  $Q_3=C-Rb45$ ,  $Q_4=N$

(Het-b)

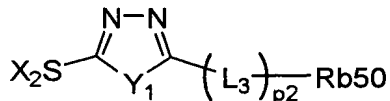


$Q_5=N$ ,  $Q_6=C-Rb48$  or  $Q_5=C-Rb48$ ,  $Q_6=N$

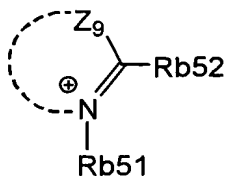
(Het-c)



(Het-d)



(Het-e)



M1m1

In the formulas, Rb43, Rb44, Rb45, Rb46, Rb47 and Rb48 each independently are a hydrogen atom or a monovalent substituent. Rb49 represents an alkyl group, an alkenyl group, an alkynyl group, an aryl group or a heterocyclic group. X<sub>1</sub> represents a hydrogen atom, an alkali metal atom, an ammonium group or a blocking group. Y<sub>1</sub> represents an oxygen atom, a sulfur atom, >NH or >N-(L<sub>4</sub>)p<sub>3</sub>-Rb53. L<sub>3</sub> and L<sub>4</sub> each represent a bivalent linking group. Rb50 and Rb53 each represent a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group, an aryl group or a heterocyclic group. X<sub>2</sub> has the same meaning as X<sub>1</sub>. p<sub>2</sub> and p<sub>3</sub> each independently are an integer of 0 to 3, preferably 1.

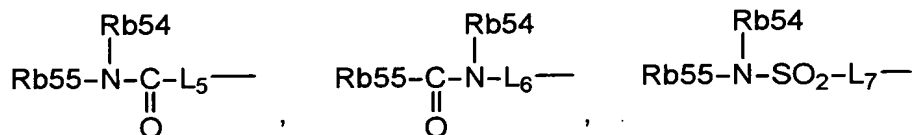
Z<sub>9</sub> represents an atomic group necessary for forming a 5- or 6-membered nitrogen-containing heterocycle. Rb51 represents an alkyl group, an alkenyl group or an alkynyl group. Rb52 represents a hydrogen atom, an alkyl group, an alkenyl group or an alkynyl group. It is to be noted that each of general formulas (Het-a) to (Het-e) is substituted with at least one -(M)k<sub>2</sub>-(Hy). Provided that -(M)k<sub>2</sub>-(Hy) does not substituted with X<sub>1</sub>, and X<sub>2</sub> of general formulas (Het-c) and (Het-d). Of general formulas (Het-a) to (Het-e), general formulas (Het-a), (Het-c) and (Het-d) are preferable, and general formula (Het-c) is more preferable.

Next, general formulas (Het-a) to (Het-e) will be

described in more detail. Rb43, Rb44, Rb45, Rb46, Rb47 and Rb48 each independently are a hydrogen atom or a monovalent substituent. Examples of the monovalent substituent include the aforementioned Rb6, Rb7, Rb8, 5 Rb9 and substituent Yy, and more preferably a lower alkyl group (preferably, those being substituted or unsubstituted and having 1-4 carbon atoms, e.g., methyl, ethyl, n-propyl, isopropyl, n-butyl, t-butyl, methoxyethyl, hydroxyethyl, hydroxymethyl, vinyl and 10 allyl), a carboxyl group, an alkoxy group (preferably, those being substituted or unsubstituted and having 1-5 carbon atoms, e.g., methoxy, ethoxy, methoxyethoxy and hydroxyethoxy), an aralkyl group (preferably, those being substituted or unsubstituted and having 7-12 15 carbon atoms, e.g., benzyl, phenethyl, and phenylpropyl), an aryl group (preferably, those being substituted or unsubstituted and having 6-12 carbon atoms, e.g., phenyl, 4-methylphenyl and 4-methoxyphenyl), a heterocyclic group (e.g., 2-pyridyl), 20 an alkylthio group (preferably, those being substituted or unsubstituted and having 1-10 carbon atoms, e.g., methylthio and ethylthio), an arylthio group (preferably, those being substituted or unsubstituted and having 6-12 carbon atoms, e.g., phenylthio), an 25 aryloxy group (preferably, those being substituted or unsubstituted and having 6-12 carbon atoms, e.g., phenoxy), an alkylamino group having three or more

carbon atoms (e.g., propylamino and butylamino), an arylamino group (e.g., anilino), a halogen atom (e.g., a chlorine atom, a bromine atom and a fluorine atom), or the following substituent.

5



Here, L5, L6 and L7 each represent a linking group represented by an alkylene group (preferably, those having 1-5 carbon atoms, e.g., methylene, propylene and 2-hydroxypropylene). Rb54 and Rb55 may be the same or different, and each represent a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group (preferably, those being substituted or unsubstituted and having 1-10 carbon atoms, e.g., methyl, ethyl, n-propyl, isopropyl, n-butyl, t-butyl, n-octyl, methoxyethyl, hydroxyethyl, allyl and propargyl), an aralkyl group (preferably, those being substituted or unsubstituted and having 7-12 carbon atoms, e.g., benzyl, phenethyl and vinylbenzyl), an aryl group (preferably, those being substituted or unsubstituted and having 6-12 carbon atoms, e.g., phenyl and 4-methylphenyl), or a heterocyclic group (e.g., 2-pyridyl).

The alkyl group, the alkenyl group, the alkynyl group, the aryl group and the heterocyclic group represented by Rb49 may be unsubstituted or substituted, and may preferably be substituents presented as Rb6, Rb7, Rb8, Rb9 and Yy.

More preferable examples include a halogen atom (e.g., a chlorine atom, a bromine atom and a fluorine atom), a nitro group, a cyano group, a hydroxyl group, an alkoxy group (e.g., methoxy), an aryl group (e.g., phenyl), an acylamino group (e.g., propionylamino), an alkoxycarbonylamino group (e.g., methoxycarbonylamino), an ureido group, an amino group, a heterocyclic group (e.g., 2-pyridyl), an acyl group (e.g., acetyl), a sulfamoyl group, a sulfonamide group, a thioureido group, a carbamoyl group, an alkylthio group (e.g., methylthio), an arylthio group (e.g., phenylthio), a heterocyclic thio group (e.g., 2-benzothiazolylthio), a carboxylic acid group, a sulfo group and salts thereof. The aforementioned ureido group, thioureido group, sulfamoyl group, carbamoyl group and amino group include those being unsubstituted, those being N-alkyl substituted and those being N-aryl substituted. Examples of the aryl group include a phenyl group and a substituted phenyl group. Examples of the substituent include the aforementioned Rb6, Rb7, Rb8, Rb9 and substituent Yy.

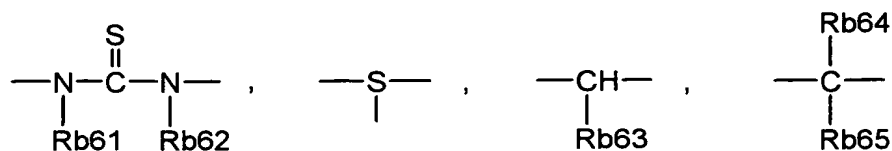
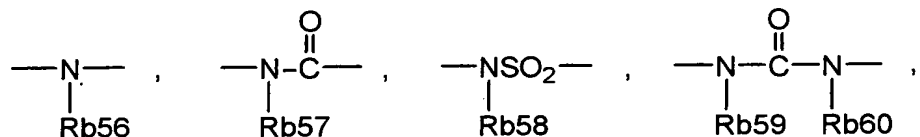
The alkali metal atom represented by X1 and X2 include a sodium atom and a potassium atom. The ammonium group include, for example, tetramethylammonium and trimethylbenzylammonium. The blocking group is a group capable of cleaving under alkaline condition. Examples of the blocking group



include acetyl, cyanoethyl and methanesulfonylethyl.

Specific examples of the bivalent linking groups represented by L<sub>3</sub> and L<sub>4</sub> include the linking group presented below or combinations of them.

5



Rb56, Rb57, Rb58, Rb59, Rb60, Rb61, Rb62, Rb63, Rb64 and Rb65 each independently represent a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group (preferably, those being substituted or  
10 unsubstituted and having 1-4 carbon atoms, e.g., methyl, ethyl, n-butyl, methoxyethyl, hydroxyethyl and allyl) or an aralkyl group (preferably, those being substituted or unsubstituted and having 7-12 carbon  
15 atoms, e.g., benzyl, phenethyl and phenylpropyl). Rb50 and Rb53 preferably are the same as those presented for the aforementioned Rb49.

Examples of the heterocyclic group having Z9 as a ring-constituting atom include thiazoliums {e.g.,  
20 thiazolium, 4-methylthiazolium, benzothiazolium, 5-methylbenzothiazolium, 5-chlorobenzothiazolium, 5-methoxybenzothiazolium, 6-methylbenzothiazolium,

6-methoxybenzothiazolium, naphtho[1,2-d]thiazolium and  
naphtho[2,1-d]thiazolium}, oxazoliums (e.g., oxazolium,  
4-methyloxazolium, benzoxazolium, 5-chlorobenzoxazolium,  
5-phenylbenzoxazolium, 5-methylbenzoxazolium and  
5 naphtho[1,2-d]oxazolium), imidazoliums (e.g.,  
1-methylbenzoimidazolium, 1-propyl-5-  
chlorobenzoimidazolium, 1-ethyl-5,6-  
cyclobenzoimidazolium and 1-allyl-5-trifluoromethyl-6-  
chloro-benzoimidazolium), and selenazoliums (e.g.,  
10 benzoselenazolium, 5-chlorobenzoselenazolium,  
5-methylbenzoselenazolium, 5-methoxybenzoselenazolium  
and naphtho[1,2-d]selenazolium. Particularly preferred  
are thiazoliums (e.g., benzothiazolium,  
5-chlorobenzothiazolium, 5-methoxybenzothiazolium and  
15 naphtho[1,2-d]thiazolium).

Preferable examples of Rb51 and Rb52 include a  
hydrogen atom, an unsubstituted alkyl group having 1-18  
carbon atoms (e.g., methyl, ethyl, propyl, butyl,  
pentyl, octyl, decyl, dodecyl and octadecyl) and a  
20 substituted alkyl group (e.g., an alkyl group having  
2-18 carbon atoms substituted with a substituent  
examples of which include a vinyl group, a carboxyl  
group, a sulfo group, a cyano group, a halogen atom  
(e.g., fluorine, chlorine and bromine), a hydroxyl  
25 group, an alkoxycarbonyl group having 1-8 carbon atoms  
(e.g., methoxycarbonyl, ethoxycarbonyl, phenoxycarbonyl  
and benzyloxycarbonyl), an alkoxy group having 1-8

carbon atoms (e.g., methoxy, ethoxy, benzyloxy and phenethyloxy), a monocyclic aryloxy group having 6-10 carbon atoms (e.g., phenoxy and p-tolyloxy), an acyloxy group having 1-3 carbon atoms (e.g., acetyloxy and propionyloxy), an acyl group having 1-8 carbon atoms (e.g., acetyl, propionyl, benzoyl and mesyl), a carbamoyl group (e.g., carbamoyl, N,N-dimethylcarbamoyl, morpholinocarbonyl and piperidinocarbonyl), a sulfamoyl group (e.g., sulfamoyl, N,N-dimethylsulfamoyl, morpholinosulfonyl and piperidinosulfonyl) and an aryl group having 6-10 (e.g., phenyl, 4-chlorophenyl, 4-methylphenyl and  $\alpha$ -naphthyl)}. It is to be noted that Rb51 is not a hydrogen atom. More preferably, Rb51 is an unsubstituted alkyl group (e.g., methyl and ethyl) or an alkenyl group (e.g., an allyl group), and Rb52 is a hydrogen atom or an unsubstituted lower alkyl group (e.g., methyl and ethyl).

M1 and m1 are included in the formula to show the presence or absence of a cation or an anion when a counter ion is necessary for neutralizing an ionic charge in the compound represented by general formula (Het-e). Whether a dye is a cation or an anion, or whether or not it has a net ionic charge depends on its auxochrome and substituent. Typical examples of such a cation include an inorganic or organic ammonium ion and alkali metal ion; while such an anion may be an inorganic or organic one, with examples including a

halogen anion (e.g., a fluoride ion, a chloride ion, a bromide ion and an iodide ion), a substituted arylsulfonate ion (e.g., a p-toluenesulfonate ion and a p-chlorobenzenesulfonate ion), an aryldisulfonate ion  
5 (e.g., a 1,3-benzenedisulfonate ion, a 1,5-naphthalenedisulfonate ion and a 2,6-naphthalenedisulfonate ion), an alkylsulfate ion (e.g., a methylsulfate ion), a sulfate ion, a thiocyanate ion, a perchlorate ion, a tetrafluoroborate ion, a picrate  
10 ion, an acetate ion and a trifluoromethanesulfonate ion. Preferable examples include an ammonium ion, an iodine ion, a bromine ion and a p-toluenesulfonate ion.

Each of the nitrogen-containing heterocycles represented by general formulas (Het-a) to (Het-e) is  
15 substituted with at least one -(M)<sub>k2</sub>-(Hy) the substitution site of which is, for example, Rb43, Rb44, Rb45, Rb46, Rb47, Rb48, Rb49, R50, Rb51, Y<sub>1</sub>, L<sub>3</sub> and Z<sub>9</sub>.

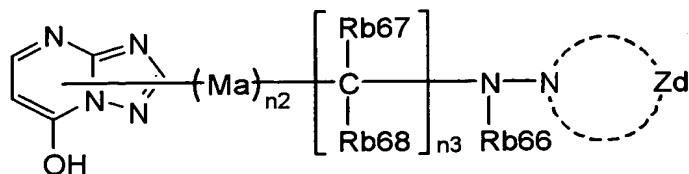
In general formula (VII), M represents a bivalent linking group comprising an atom or atomic group  
20 containing at least one of a carbon atom, a nitrogen atom, a sulfur atom and an oxygen atom, and preferably represents a bivalent linking group having 4-20 carbon atoms made up of an alkylene group having 1-8 carbon atoms (e.g., methylene, ethylene, propylene, butylene  
25 and pentylene), an arylene group having 6-12 carbon atoms (e.g., phenylene and naphthylene), an alkenylene group having 2-8 carbon atoms (e.g., ethynylene and

propenylene), an amide group, an ester group,  
a sulfoamide group, a sulfonic acid ester group,  
an ureido group, a sulfonyl group, a sulfinyl group,  
a thioether group, an ether group, a carbonyl group,  
5 -N(R0)- (wherein R0 represents a hydrogen atom,  
a substituted or unsubstituted alkyl group or  
a substituted or unsubstituted aryl group) or  
a heterocyclic divalent group (e.g., 6-chloro-1,3,5-  
triazin-2,4-diyl, pyrimidin-2,4-diyl, quinoxalin-2,3-  
10 diyl) individually or in combination of two or more  
thereof. More preferably, M is an ureido group, an  
ester group or an amide group.

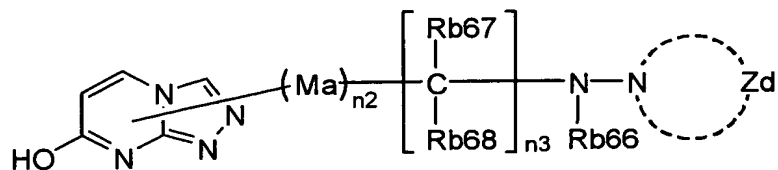
In general formula (VII), k1 and k3 each  
preferably are 1 or 2. It is more preferable that all  
15 of k1, k2 and k3 are 1. When k1 or k3 is 2 or more, Hy  
and Het may be the same or different.

Of the compounds represented by general formula  
(VII) of the present invention, more preferable  
compounds are represented by the following general  
20 formulas (VII-A), (VII-B), (VII-C), (VII-D) and  
(VII-E):

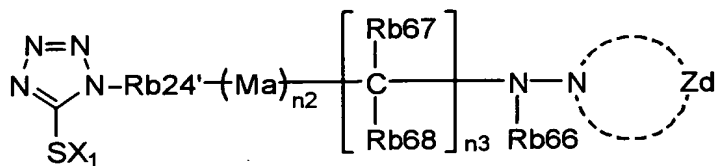
(VII-A)



(VII-B)

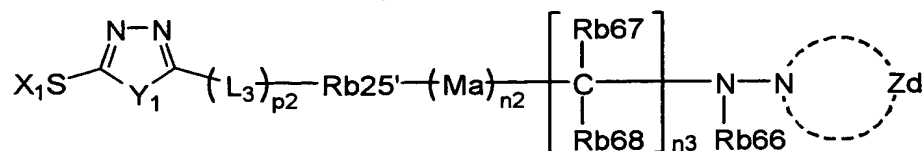


(VII-C)



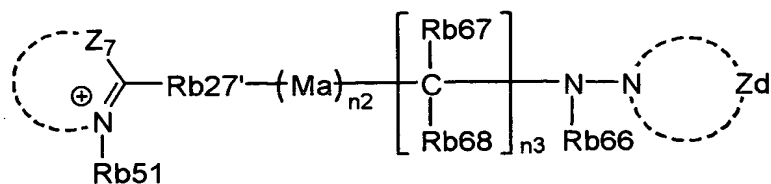
Rb24' represents an alkylene group, arylene group or bivalent heterocyclic group

(VII-D)



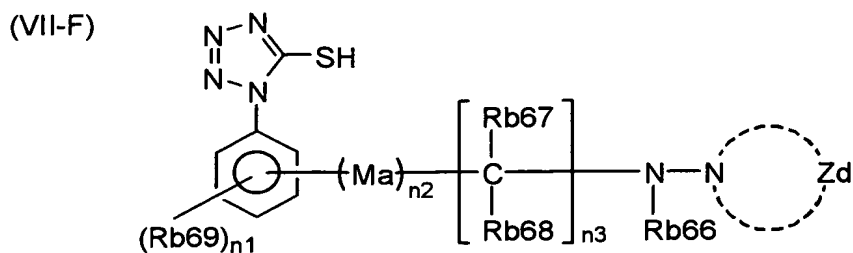
Rb25' has the same meaning as Rb24'

(VII-E)



Rb27' represents an alkylene group

Further, the compounds particularly preferable in the present invention are represented by the following general formula (VII-F):



In the formulas, Ma has the same meaning as M in general formula (VII). Zd has the same meaning as Z4 in general formula (Hy-1). Rb59 represents a monovalent substituent. Rb66 represents an alkyl group, an alkenyl group, an alkynyl group, an aryl group or a heterocyclic group. Rb67 and Rb68 each independently represent a hydrogen atom or a monovalent substituent.

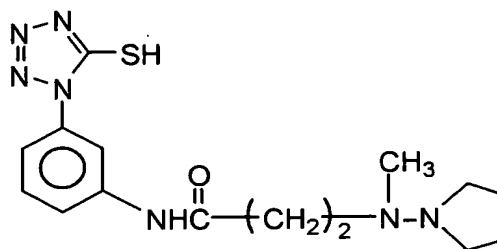
n1 represents an integer of 0 to 4. n2 represents 0 or 1. n3 represents an integer of 1 to 6. X<sub>1</sub> has the same meaning as X<sub>1</sub> in general formula (Het-c). Y<sub>1</sub>, L<sub>3</sub> and p2 have the same meanings as Y<sub>1</sub>, L<sub>3</sub> and p2 in general formula (Het-d), respectively. Rb51 has the same meaning as Rb51 in general formula (Het-e). when n1 and n3 are 2 or more, Rb59 and C(Rb67)(Rb68) are repeated, but they are not required to be the same.

Describing in more detail, it is preferable that Ma is the same as M in general formula (VII), and more preferably an ureido group, an ester group or an amide group. Zd is preferably the same as Z<sub>4</sub> in general formula (Hy-1), and more preferably an unsubstituted tetramethylene or pentamethylene group. Rb69 is preferably the same as Rb43. Rb66 is preferably the same as Rb6, Rb7, Rb8 and Rb9, and particularly

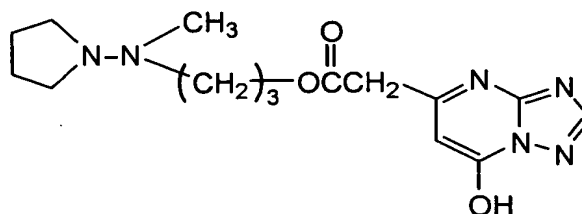
preferably an unsubstituted alkyl group having 1-4 carbon atoms (e.g., methyl and ethyl). Rb67 and Rb68 are preferably the same as Rb43, and particularly preferably a hydrogen atom. n1 is preferably 0 or 1.  
 5 n2 is preferably 1. n3 is preferably 2 to 4.

Compounds to be used in the present invention are typically exemplified by, but are not limited to, the following:

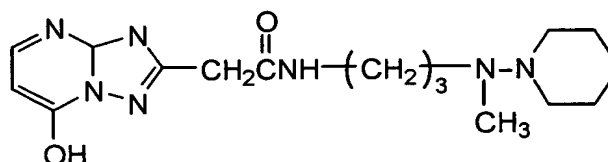
VII-1



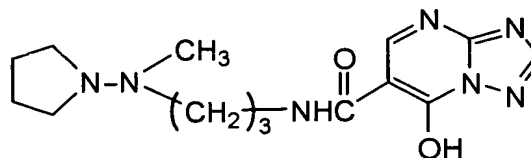
VII-2



VII-3

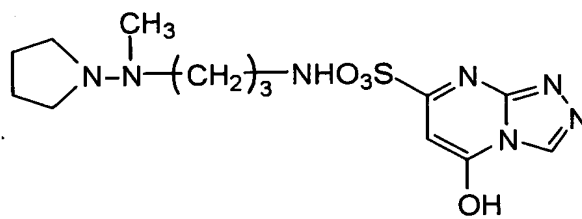


VII-4

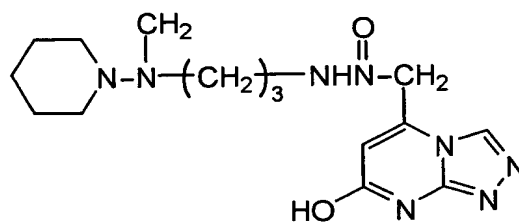




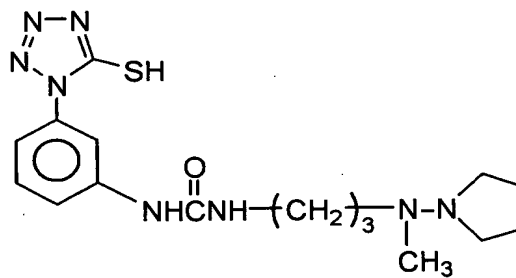
VII-5



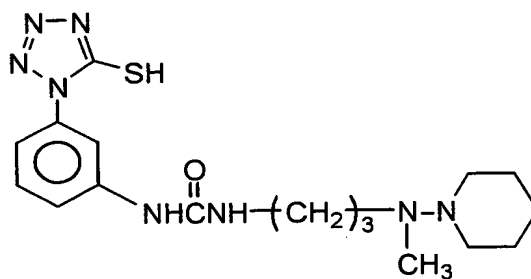
VII-6

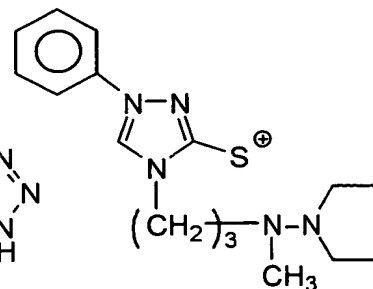
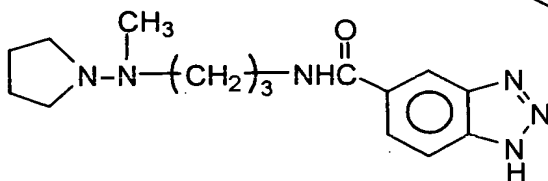
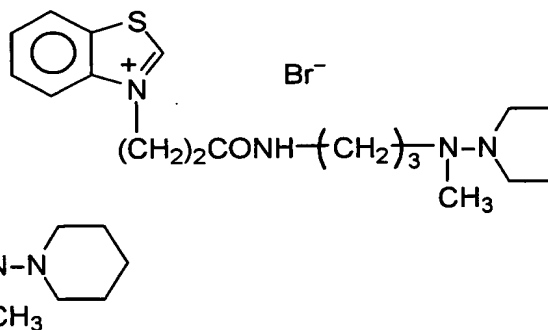
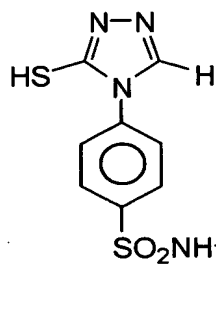
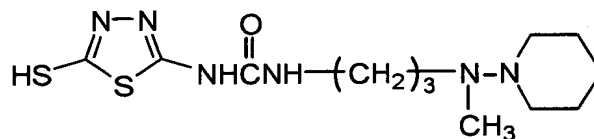
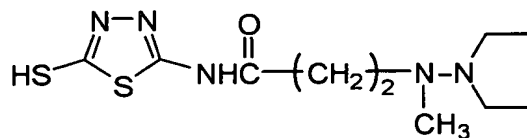
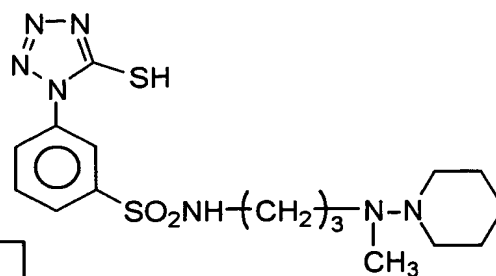
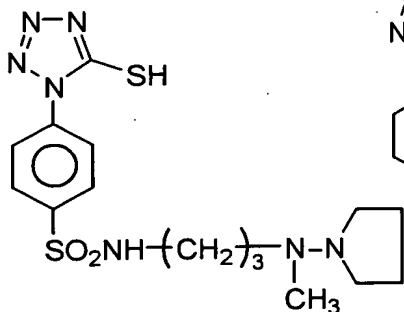


VII-7



VII-8





Het in general formula (VII) used in the present invention is disclosed in, for example, U.S.P. No. 3,266,897, Belgian Patent No. 671,402, JP-A-60-138548, JP-A-59-68732, JP-A-59-123838, JP-B-58-9939, JP-A-59-137951, JP-A-57-202531, JP-A-57-164734, JP-A-57-14836, JP-A-57-116340, U.S.P. No. 4,418,140, JP-A-58-95728, JP-A-55-79436, OLS No. 2,205,029, OLS No. 1,962,605, JP-A-55-59463, JP-B-48-18257, JP-B-53-28084, JP-A-53-48723, JP-B-59-52414, JP-A-58-217928, JP-B-49-8334, U.S.P. No. 3,598,602, U.S.P. No. 887,009, U.K.P. No. 965,047, Belgian Patent No. 737809, U.S.P. No. 3,622,340, JP-A-60-87322, JP-A-57-211142, JP-A-58-158631, JP-A-59-15240, U.S.P. No. 3,671,255, JP-B-48-34166, JP-B-48-322112, JP-A-58-221839, JP-B-48-32367, JP-A-60-130731, JP-A-60-122936, JP-A-60-117240, U.S.P. No. 3,228,770, JP-B-43-13496, JP-B-43-10256, JP-B-47-8725, JP-B-47-30206, JP-B-47-4417, JP-B-51-25340, U.K.P. No. 1,165,075, U.S.P. No. 3,512,982, U.S.P. No. 1,472,845, JP-B-39-22067, JP-B-39-22068, U.S.P. No. 3,148,067, U.S.P. No. 3,759,901, U.S.P. No. 3,909,268, JP-B-50-40665, JP-B-39-2829, U.S.P. No. 3,148,066, JP-B-45-22190, U.S.P. No. 1,399,449, U.K.P. No. 1,287,284, U.S.P. No. 3,900,321, U.S.P. No. 3,655,391, U.S.P. No. 3,910,792, U.K.P. No. 1,064,805, U.S.P. No. 3,544,336, U.S.P. No. 4,003,746, U.K.P. No. 1,344,525, U.K.P. No. 972,211, JP-B-43-4136, U.S.P. No. 3,140,178, French Patent No. 2,015,456, U.S.P. No. 3,114,637, Belgian

Patent No. 681,359, U.S.P. No. 3,220,839, U.K.P. No.  
1,290,868, U.S.P. No. 3,137,578, U.S.P. No. 3,420,670,  
U.S.P. No. 2,759,908, U.S.P. No. 3,622,340, OLS No.  
2,501,261, DAS No. 1,772, 424, U.S.P. No. 3,157,509,  
5 French Patent No. 1,351,234, U.S.P. No. 3,630,745,  
French Patent No. 2,005,204, German Patent No.  
1,447,796, U.S.P. No. 3,915,710, JP-B-49-8334, U.K.P.  
No. 1,021,199, U.K.P. No. 919,061, JP-B-46-17513, U.S.P.  
No. 3,202,512, OLS No. 2,553,127, JP-A-50-104927,  
10 French Patent No. 1,467,510, U.S.P. No. 3,449,126,  
U.S.P. No. 3,503,936, U.S.P. No. 3,576,638, French  
Patent No. 2,093,209, U.K.P. No. 1,246,311, U.S.P. No.  
3,844,788, U.S.P. No. 3,535,115, U.K.P. No. 1,161,264,  
U.S.P. No. 3,841,878, U.S.P. No. 3,615,616, JP-A-48-  
15 39039, U.K.P. No. 1,249,077, JP-B-48-34166, U.S.P. No.  
3,671,255, U.K.P. No. 1459160, JP-A-50-6323, U.K.P. No.  
1,402,819, OLS No. 2,031,314, Research Disclosure No.  
13651, U.S.P. No. 3,910,791, U.S.P. No. 3,954,478,  
U.S.P. No. 3,813,249, U.K.P. No. 1,387,654, JP-A-57-  
20 135945, JP-A-57-96331, JP-A-57-22234, JP-A-59-26731,  
OLS No. 2,217,153, U.K.P. No. 1,394,371, U.K.P. No.  
1,308,777, U.K.P. No. 1,389,089, U.K.P. No. 1,347,544,  
German Patent No. 1,107,508, U.S.P. No. 3,386,831,  
U.K.P. No. 1,129,623, JP-A-49-14120, JP-B-46-34675, JP-  
25 A-50-43923, U.S.P. No. 3,642,481, U.K.P. No. 1,269,268,  
U.S.P. No. 3,128,185, U.S.P. No. 3,295,981, U.S.P. No.  
3,396,023, U.S.P. No. 2,895,827, JP-B-48-38418, JP-A-

48-47335, JP-A-50-87028, U.S.P. No. 3,236,652, U.S.P.  
No. 3,443,951, U.K.P. No. 1,065,669, U.S.P. No.  
3,312,552, U.S.P. No. 3,310,405, U.S.P. No. 3,300,312,  
U.K.P. No. 952,162, U.K.P. No. 952,162, U.K.P. No.  
5 948,442, JP-A-49-120628, JP-B-48-35372, JP-B-47-5315,  
JP-B-39-18706, JP-B-43-4941, and JP-A-59-34530. That  
compound can be synthesized by referring to them.

Hy in general formula (VII) of the present  
invention can be prepared by various methods. For  
10 example, it can be prepared by a method in which a  
hydrazine is alkylated. The known methods for the  
alkylation include a method in which hydrazine is  
substitution alkylated using alkyl halide and alkyl  
sulfonate, a method in which hydrazine is reductively  
15 alkylated using a carbonyl compound and sodium  
cyanoborohydride, and a method in which hydrazine is  
acylated and thereafter reduced with lithium aluminum  
hydride. For example, these methods are disclosed in  
S. R. Sandler, W. Karo, "Organic Functional Group  
20 Preparation" Volume 1, Chapter 14, pp. 434-465,  
Academic Press (1968); E. L. Clennan et al, Journal of  
The American Chemical Society, Vol. 112, No. 13, 5080  
(1990), and so on. That compound can be prepared by  
referring to them.

25 For bond formation reactions such as an amide bond  
formation reaction and an ester bond formation reaction  
of the  $-(M)k_2-(Hy)$  moiety, methods known in organic

chemistry can be utilized. Specifically, any method can be applied such as a method in which Het and Hy are connected, a method in which Hy is connected to a synthesis raw material and an intermediate of Het and thereafter Het is synthesized and a method in which a synthesis raw material and an intermediate of Hy are connected to an Het moiety and thereafter Hy is synthesized. The synthesis can be performed through a suitable selection. With respect to these synthesis reactions for connection, reference should be made to the literature regarding organic synthetic reaction, for example, Japanese Chemical Society Ed., New Experimental Chemistry Series No. 14, Synthesis and Reaction of Organic Compounds, Vols. I to V, Maruzene, Tokyo, 1977; Yoshiro Ogata, "The Theory of Organic Reaction," Maruzene, Tokyo, 1962; and L. F. Fieser and M. Fieser, "Advanced Organic Chemistry," Maruzene, Tokyo, 1962. More specifically, the synthesis can be performed according to the methods described in Examples 1 and 2 in JP-A-7-135341.

When a compound is added in the preparation of an emulsion, this compound can be added at any point during the preparation. For example, the compound can be added during silver halide grain formation, before or during desalting, before or during chemical ripening, or before the preparation of a complete emulsion. The compound can also be added separately a plurality of

times during these steps. The compound represented by general formula (VII) of the present invention is preferably added after being dissolved in any of water, a water-soluble solvent such as methanol and ethanol, and a solvent mixture of these. When a compound is dissolved in water, if the compound becomes to exhibit an increased solubility when the pH is raised or lowered, it can be added after being dissolved through the raising or lowering of the pH.

The compounds represented by general formula (VII) are preferably used for an emulsion layer, but they may be added to a protective layer and an intermediate layer as well as an emulsion layer previously and then be caused to diffuse during application. The timing of their addition of the compound represented by general formula (VII) of the present invention may be either before or after the addition of a sensitizing dye. Those compounds are caused to be contained in a silver halide emulsion in a ratio of  $1 \times 10^{-9}$  to  $5 \times 10^{-2}$  mol, preferably  $1 \times 10^{-8}$  to  $2 \times 10^{-3}$  mol, per mol of the silver halide.

The compounds represented by general formulas (VIII-1) and (VIII-2) will be described in detail below. In general formula (VII-1), examples of the substituents represented by Rb10, Rb11, Rb12 and Rb13 include an alkyl group (preferably having 1-30 carbon atoms, more preferably 1-20 carbon atoms, e.g., methyl,

ethyl and iso-propyl), an aralkyl group (preferably having 7-30 carbon atoms, more preferably 7-20 carbon atoms, e.g., phenylmethyl), an alkenyl group (preferably having 2-20 carbon atoms, more preferably 2-10 carbon atoms, e.g., allyl), an alkoxy group (preferably having 1-20 carbon atoms, more preferably 1-10 carbon atoms, e.g., methoxy and ethoxy), an aryl group (preferably having 6-30 carbon atoms, more preferably 6-20 carbon atoms), an acylamino group (preferably having 2-30 carbon atoms, more preferably 2-20 carbon atoms, e.g., acetylamino), a sulfonylamino group (preferably having 1-30 carbon atoms, more preferably 1-20 carbon atoms, e.g., methanesulfonylamino), an ureido group (preferably having 1-30 carbon atoms, more preferably 1-20 carbon atoms, e.g., methylureido), an alkoxycarbonylamino group (preferably having 2-30 carbon atoms, more preferably 2-20 carbon atoms, e.g., methoxycarbonylamino), an aryloxycarbonylamino group (preferably having 7-30 carbon atoms, more preferably 7-20 carbon atoms, e.g., a phenyloxycarbonylamino group), an aryloxy group (preferably having 6-30 carbon atoms, more preferably 6-20 carbon atoms, e.g., phenyloxy), a sulfamoyl group (preferably having 0-30 carbon atoms, more preferably 0-20 carbon atoms, e.g., methylsulfamoyl), a carbamoyl group (preferably having 1-30 carbon atoms, more preferably 1-20 carbon atoms,



e.g., carbamoyl and methylcarbamoyl), a mercapto group, an alkylthio group (preferably having 1-30 carbon atoms, more preferably 1-20 carbon atoms, e.g., methylthio and carboxymethylthio), an arylthio group (preferably  
5 having 6-30 carbon atoms, more preferably 6-20 carbon atoms, e.g., phenylthio), a sulfonyl group (preferably having 1-30 carbon atoms, more preferably 1-20 carbon atoms, e.g., methanesulfonyl), a sulfinyl group (preferably having 1-30 carbon atoms, more preferably  
10 1-20 carbon atoms, e.g., methanesulfinyl), a hydroxyl group, a halogen atom (e.g., a chlorine atom, a bromine atom and a fluorine atom), a cyano group, a sulfo group, a carboxyl group, a phosphono group, an amino group (preferably having 0-30 carbon atoms, more preferably  
15 1-20 carbon atoms, e.g., methylamino), an aryloxy carbonyl group (preferably having 7-30 carbon atoms, more preferably 7-20 carbon atoms), an acyl group (preferably having 2-30 carbon atoms, more preferably 2-20 carbon atoms, e.g., acetyl and benzoyl),  
20 an alkoxycarbonyl group (preferably having 2-30 carbon atoms, more preferably 2-20 carbon atoms, e.g., methoxycarbonyl), an acyloxy group (preferably having 2-30 carbon atoms, more preferably 2-20 carbon atoms, e.g., acetoxy), a nitro group, a hydroxamic acid group,  
25 and a heterocyclic group (e.g., pyridyl, furyl and thienyl). These substituents may further be substituted.

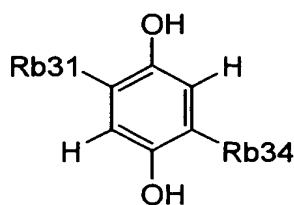
Preferable examples of the substituents represented by Rb10, Rb11, Rb12 and Rb13 include an alkyl group, an alkoxy group, a hydroxyl group, a halogen atom, a sulfo group, a carboxyl group, an acylamino group, a sulfonylamino group, an ureido group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, an alkylthio group, an arylthio group, an amino group and an acyloxy group, more preferably an alkyl group, an alkoxy group, a halogen atom, a sulfo group, a carboxyl group, an acylamino group, a sulfonylamino group, an ureido group, an alkoxycarbonylamino group and an aryloxycarbonylamino group, and particularly preferably an alkyl group, a halogen atom, an acylamino group, a sulfonylamino group, an ureido group, an alkoxycarbonylamino group and an aryloxycarbonylamino group.

Preferably, from one to three of Rb10, Rb11, Rb12 and Rb13 are each a hydrogen atom, and more preferably, from two to three of Rb10, Rb11, Rb12 and Rb13 are each a hydrogen atom. The most preferable is the case where three of them are each a hydrogen atom. When Rb10 and Rb13 are each an alkyl group, they are not substituents having the same numbers of carbon atoms. For example, it is possible that Rb10 = t-C<sub>8</sub>H<sub>17</sub> and Rb13 = n-C<sub>15</sub>H<sub>31</sub>, but it is impossible that both Rb10 and Rb13 are t-C<sub>8</sub>H<sub>17</sub>. When Rb10 and Rb13 are substituents of the same type, the difference in the number of carbon atoms

between Rb10 and Rb13 is preferably 5 or more, and more preferably 10 or more. What described above for Rb10 and Rb13 is applied equally to Rb11 and R 12.

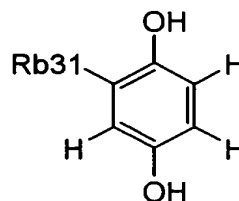
Among the compounds represented by general formula (VIII-b), those represented by general formula (VIII-1-a) are preferable, and those represented by general formula (VIII-1-b) are more preferable. The compounds represented by general formula (VIII-1-c) are particularly preferable.

(VIII-1-a)



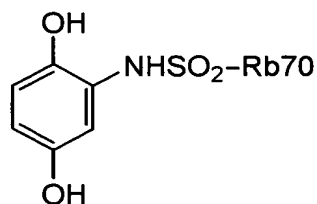
In the above formula, Rb31 and Rb34 have the same meanings as Rb10 and Rb13 of general formula (VIII-1) and their preferable ranges are also the same as those of Rb10 and Rb13.

(VIII-1-b)



In the above formula, Rb31 has the same meaning as Rb10 of general formula (VIII-1) and its preferable range is also the same as that of Rb10.

(VIII-1-c)



In the above formula, Rb70 is an alkyl group that may have a substituent. As the substituent the alkyl group may have, those presented as substituents represented by Rb31 can be applied.

5           In general formula (VIII-2), examples of substituents represented by Rb14, Rb15 and Rb16 include the substituents that the substituents represented by Rb10, Rb11, Rb12 and Rb13 may have. Preferable examples of the substituent represented by Rb14 include  
10           an alkyl group, an alkoxy group, a hydroxyl group, a halogen atom, a sulfo group, a carboxyl group, an acylamino group, a sulfonylamino group, an ureido group, an alkoxycarbonylamino group, an aryloxycarbonylamino group, an alkylthio group, an arylthio group, an amino  
15           group and an acyloxy group, more preferably include an alkyl group, an alkoxy group, a halogen atom, a sulfo group, a carboxyl group, an acylamino group, a sulfonylamino group, an ureido group, an alkoxycarbonylamino group and an aryloxycarbonylamino  
20           group, and particularly preferably include an alkyl group, a halogen atom, an acylamino group, a sulfonylamino group, an ureido group, an alkoxycarbonylamino group and an aryloxycarbonylamino group.

25           Preferable examples of the substituent represented by Rb15 include an alkyl group, an alkoxy group, a hydroxyl group, a halogen atom, an acylamino group, a

sulfonylamino group, an ureido group, an  
alkoxycarbonylamino group, an aryloxycarbonylamino  
group, an alkylthio group, an arylthio group, an amino  
group and an acyloxy group, more preferably include an  
5 alkyl group, an alkoxy group, a hydroxyl group, an  
acylamino group, a sulfonylamino group, an ureido group,  
an alkoxycarbonylamino group and an  
aryloxycarbonylamino group, and particularly preferably  
include an alkyl group, an acylamino group, a  
10 sulfonylamino group, an ureido group, an  
alkoxycarbonylamino group and an aryloxycarbonylamino  
group.

Preferable examples of the substituent represented  
by Rb16 include an alkyl group, an alkoxy group, a  
15 hydroxyl group, a halogen atom, a sulfo group, a  
carboxyl group, an acylamino group, a sulfonylamino  
group, an ureido group, an alkoxycarbonylamino group,  
an aryloxycarbonylamino group, an alkylthio group, an  
arylthio group, an amino group and an acyloxy group,  
20 more preferably include an alkyl group, an alkoxy group,  
a halogen atom, a sulfo group, a carboxyl group, an  
acylamino group, a sulfonylamino group, an ureido group,  
an alkoxycarbonylamino group and an  
aryloxycarbonylamino group, and particularly preferably  
25 include an alkyl group.

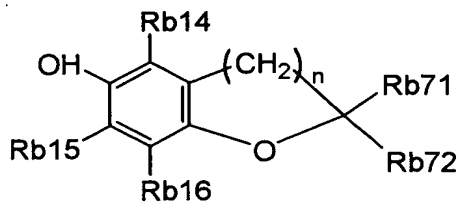
Z represents a group of non-metallic atoms  
required to form a 4- to 6-membered ring. Preferable

examples of such a non-metallic atom include a carbon atom, an oxygen atom, a nitrogen atom and a sulfur atom, more preferably a carbon atom and an oxygen atom, and particularly preferably a carbon atom. The preferable number of ring members is 5 or 6, and more preferably 6. The ring may have a substituent thereon and, for example, those presented as the substituent represented by Rb14 can be applied as such a substituent.

Preferable examples of such a substituent include an alkyl group, an alkenyl group and an alkoxy group, more preferably an alkyl group and an alkenyl group. These substituents may further have a substituent.

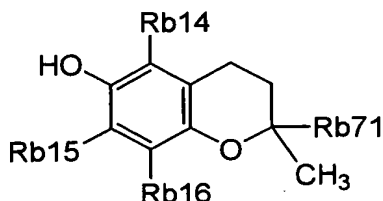
Among the compounds represented by general formula (VIII-2), preferred are the compounds represented by general formula (VIII-2-a), and more preferred are the compounds represented by general formula (VIII-2-b).

(VIII-2-a)



In the formula, Rb14, Rb15 and Rb16 have the same meanings as those in general formula (VIII-2), and their preferable ranges are also the same as those of Rb14, Rb15 and Rb16 in general formula (VIII-2).  $n$  represents 1 or 2. Rb71 and Rb72 each represent an alkyl group, an alkenyl group or an alkoxy group.

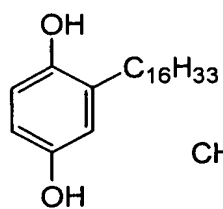
(VIII-2-b)



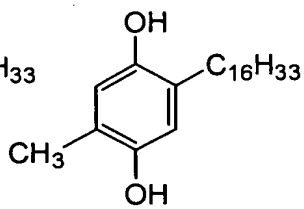
In the formula, Rb14, Rb15 and Rb16 have the same meanings as those in general formula (VIII-2), and their preferable ranges are also the same as those of Rb14, Rb15 and Rb16 in general formula (VIII-2). Rb71 represents an alkyl group, an alkenyl group or an alkoxy group. n is preferably 2. The alkyl group and the alkenyl group represented by Rb71 and Rb72 may be straight chain, branched or cyclic, and preferably is straight chain or branched. The preferable number of carbon atoms is from 1 to 30, and more preferably from 1 to 20. Examples of the alkyl group include methyl, ethyl and iso-propyl. As the alkenyl group, allyl is presented. With respect to the alkoxy groups represented by Rb71 and Rb72, their alkyl moieties may be straight chain, branched or cyclic. Further, Rb71 and Rb72 may form a ring like a spirochroman. The alkoxy group preferably has 1-20 carbon atoms and more preferably has 1-10 carbon atoms. Examples thereof include methoxy and ethoxy.

The compounds represented by general formulas (VIII-1) and (VIII-2) are specifically exemplified by, but are not restricted to, the following:

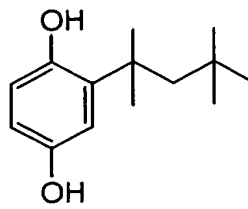
VIII-1-1



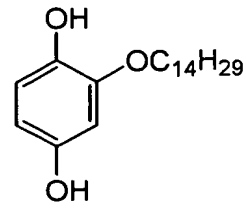
VIII-1-2



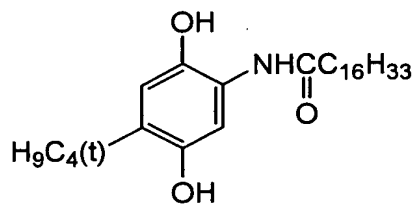
VIII-1-3



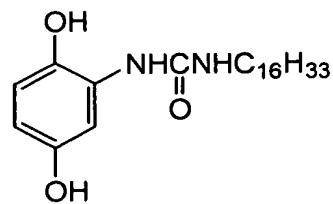
VIII-1-4



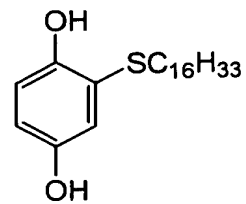
VIII-1-5



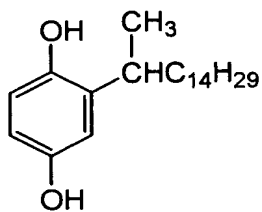
VIII-1-6



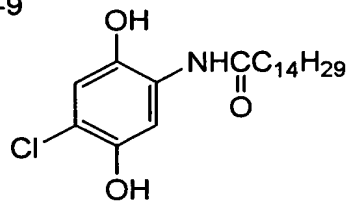
VIII-1-7



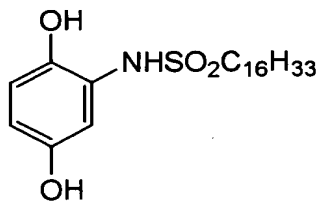
VIII-1-8



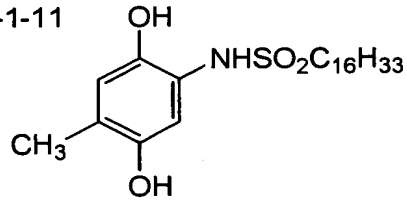
VIII-1-9



VIII-1-10

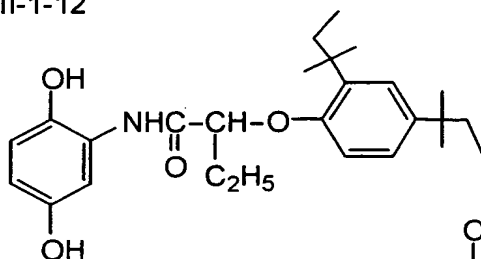


VIII-1-11

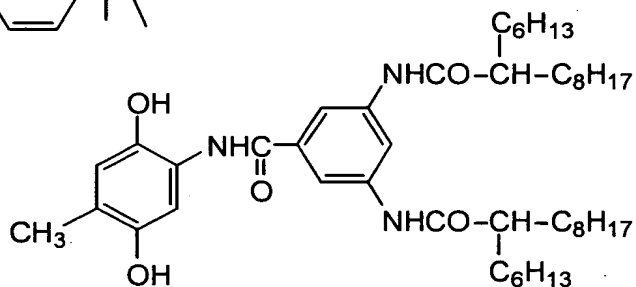




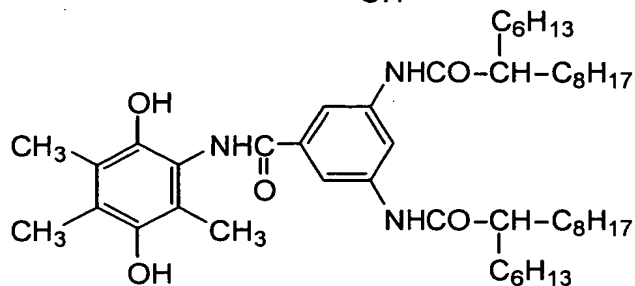
VIII-1-12



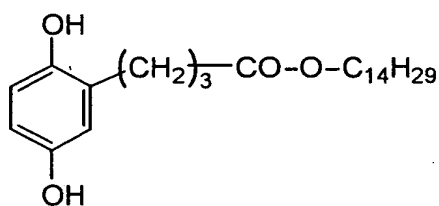
VIII-1-13



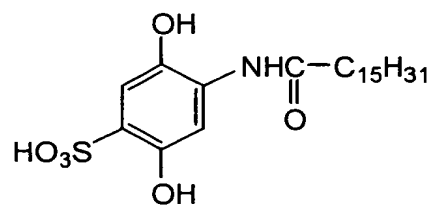
VIII-1-14



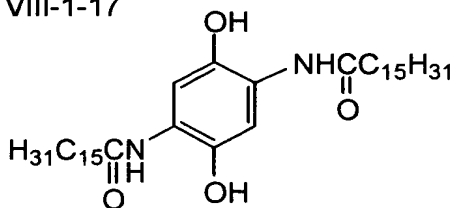
VIII-1-15



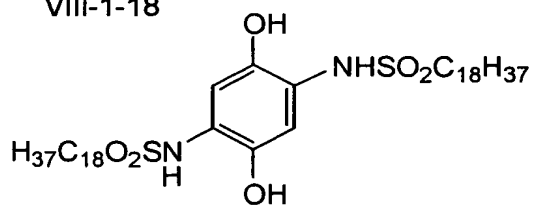
VIII-1-16



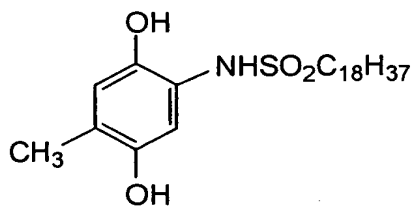
VIII-1-17



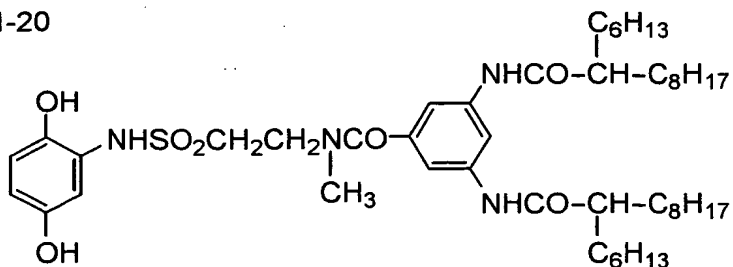
VIII-1-18



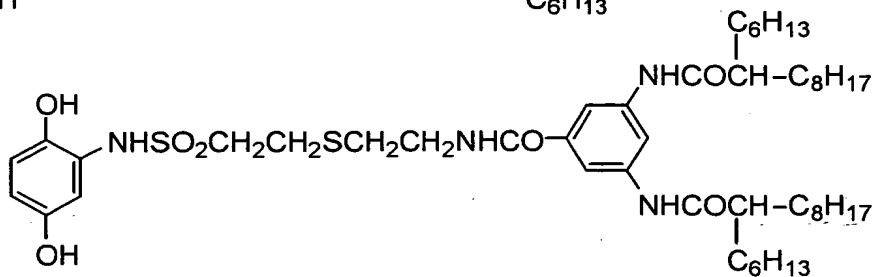
VIII-1-19



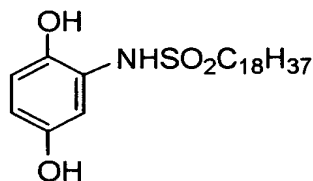
VIII-1-20



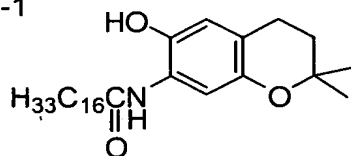
VIII-1-21



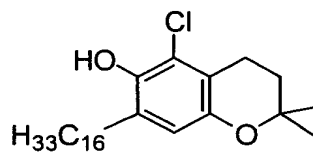
VIII-1-22



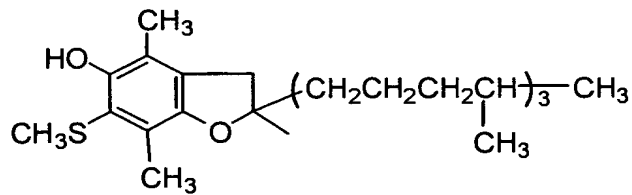
VIII-2-1



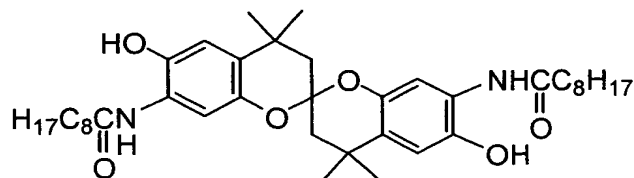
VIII-2-2



VIII-2-3



VIII-2-4



The compounds represented by general formulas (VIII-1) and (VIII-2) can be prepared according to the methods described in, for example, U.S.P. Nos.

2,728,659, 2,549,118 and 2,732,300, Journal of American  
5 Chemical Society, 111, 20, 1989, 7932, Synthesis, 12,  
1995, 1549, Q. J. Pharm, Pharmacol., 17, 1944, 325,  
Chem. Pharm, Bull., 14, 1966, 1052, and Chem. Pharm,  
Bull., 16, 1968, 853.

The compounds represented by general formulas  
10 (VIII-1) and (VIII-2) can be prepared according to the  
methods described in, for example, U.S.P. Nos.

2,421,811, 2,421, 812, 2,411,967 and 2,681,371, J. Amer.  
Chem. Soc., 65, 1943, 1276, J. Amer. Chem. Soc., 65,  
1943, 1281, J. Amer. Chem. Soc., 63, 1941, 1887, J.  
15 Amer. Chem. Soc., 107, 24, 1985, 7053, Helv. Chim.  
Acta., 21, 1938, 939, Helv. Chim. Acta., 28, 1945, 438,  
Chem. Ber., 71, 1938, 2637, J. Org. Chem., 4, 1939, 311,  
J. Org. Chem., 6, 1941, 229, J. Chem. Soc., 1938, 1382,  
Helv. Chim. Acta., 21, 1931, 1234, Tetrahedron Lett.,  
20 33, 26, 1992, 3795, J. Chem. Soc. Perkin. Trans. 1,  
1981, 1437, and Synthesis, 6, 1995, 693.

The compounds represented by formulas (VIII-1) and  
(VIII-2) are preferably added after being formed into  
an emulsified dispersion by a known dispersing method.

25 When emulsifying and dispersing those compounds, it is  
possible to cause them to coexist with additives  
generally used in the photograph industry such as dye-

forming couplers and high-boiling organic solvents.  
The compounds may be added as a fine crystal dispersion.

The addition amounts of the compounds represented  
by general formulas (VIII-1) and (VIII-2) are each  $5 \times$   
5  $10^{-4}$  to 1 mol, and preferably  $1 \times 10^{-3}$  to  $5 \times 10^{-1}$  mol,  
per mol of silver halide in the emulsion layers to  
which they are added.

With respect to the combination of the compound of  
general formula (VII) and the compound of (VIII-1) or  
10 (VIII-2), preferred is the combination of the compound  
represented by general formula (VII-F) and the compound  
represented by general formula (VIII-1-b) or (VIII-2).

In the present invention, the compound represented  
by general formula (VII), a compound selected from the  
15 group consisting of the compounds represented by  
general formulas (VIII-1) and (VIII-2), and a compound  
selected from the group consisting of the compounds  
represented by general formulas (IX-1), (IX-2) and (X)  
may be added to the same layer or to separate layers.

20 The compound represented by general formula (IX-1)  
will be described in more detail. In the formula, the  
alkyl group is a straight chain, branched or cyclic  
alkyl group that may have a substituent. In general  
formula (IX-1), R<sub>1</sub> represents a substituted or  
25 unsubstituted alkyl group (preferably, an alkyl group  
having 1-13 carbon atoms, e.g., methyl, ethyl, i-propyl,  
cyclopropyl, butyl, isobutyl, cyclohexyl, t-octyl,

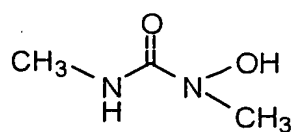
decyl, dodecyl, hexadecyl and benzyl), a substituted or unsubstituted alkenyl group (preferably, an alkenyl group having 2-14 carbon atoms, e.g., allyl, 2-butenyl, isopropenyl, oleyl and vinyl), and a substituted or unsubstituted aryl group (preferably, an aryl group having 6-14 carbon atoms, e.g., phenyl and naphthyl). Rc2 represents a hydrogen atom or the groups presented for Rc1. Rc3 is a hydrogen atom or a substituted or unsubstituted alkyl group having 1-10 carbon atoms (e.g., methyl, i-butyl and cyclohexyl) or a substituted or unsubstituted an alkenyl group (e.g., vinyl and i-propenyl). The total of the numbers of the carbon atoms contained in Rc1, Rc2 and Rc3 is 20 or less, and preferably 12 or less. Examples of substituents when Rc1 to Rc3 are substituted groups include a hydroxyl group, an alkoxy group, an aryloxy group, a silyl group, a silyloxy group, an alkylthio group, an arylthio group, an amino group, an acylamino group, a sulfonamide group, an alkylamino group, an arylamino group, a carbamoyl group, a sulfamoyl group, a sulfo group, a carboxyl group, a halogen atom, a cyano group, a nitro group, a sulfonyl group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, an acyloxy group, a hydroxyamino group and a heterocyclic group. Rc1 and Rc3, or Rc2 and Rc3 may be bonded together to form a 5- to 7-membered ring.

Among the compounds represented by general formula

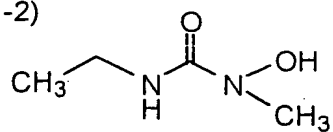
(IX-1), preferred are compounds having the total number of carbon atoms is 20 or less, more preferably 12 or less.

5       The following are specific examples of the compound represented by general formula (IX-1), but the present invention is not restricted to them.

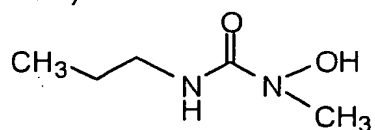
(IX-1-1)



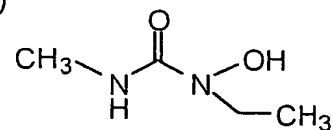
(IX-1-2)



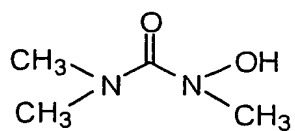
(IX-1-3)



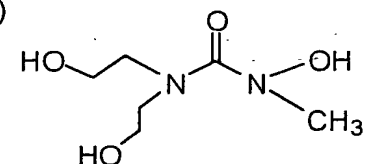
(IX-1-4)



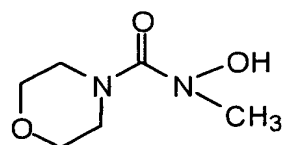
(IX-1-5)



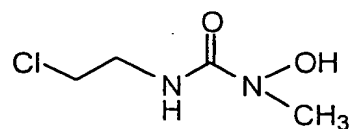
(IX-1-6)



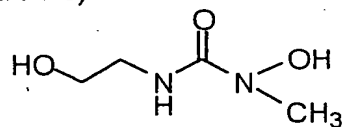
(IX-1-7)



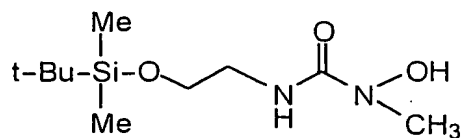
(IX-1-8)



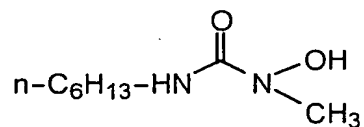
(IX-1-9)



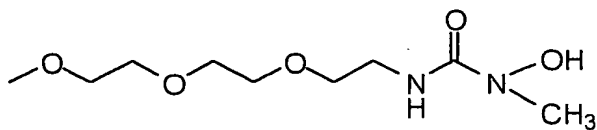
(IX-1-10)



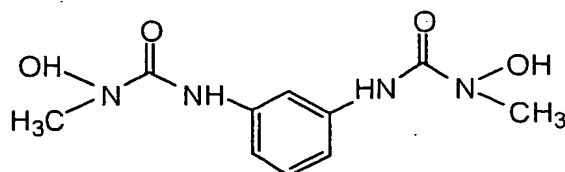
(IX-1-11)



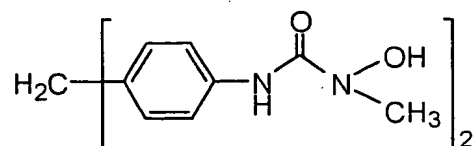
(IX-1-12)



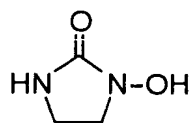
(IX-1-13)



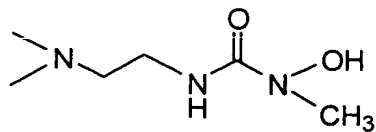
(IX-1-14)



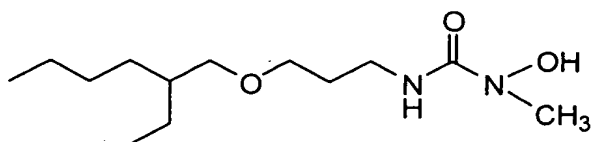
(IX-1-15)



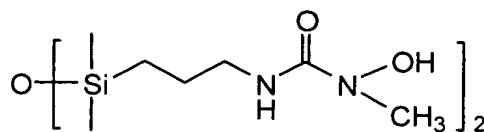
(IX-1-16)



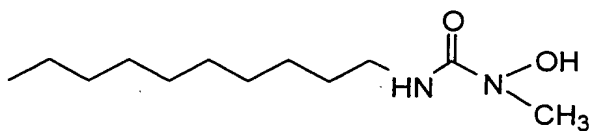
(IX-1-17)



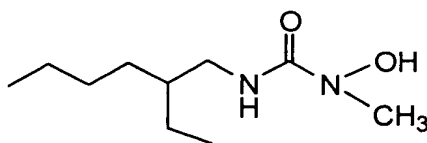
(IX-1-18)



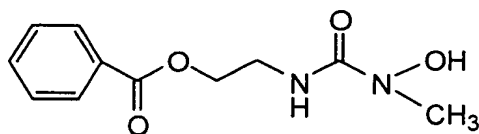
(IX-1-19)



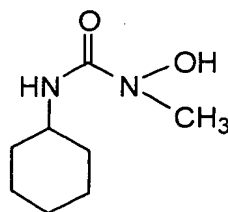
(IX-1-20)



(IX-1-21)

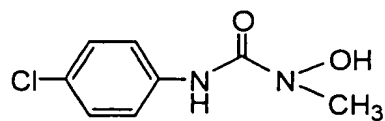


(IX-1-22)

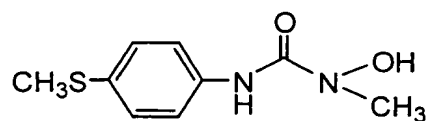




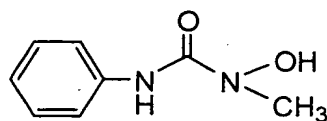
(IX-1-23)



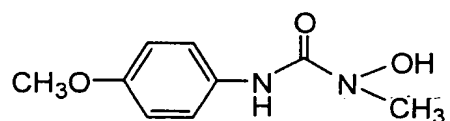
(IX-1-24)



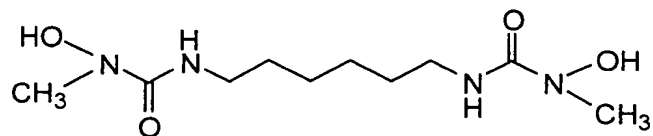
(IX-1-25)



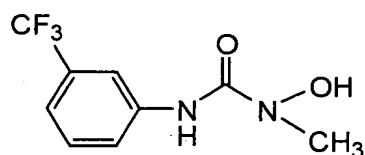
(IX-1-26)



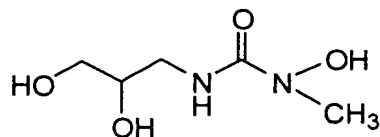
(IX-1-27)



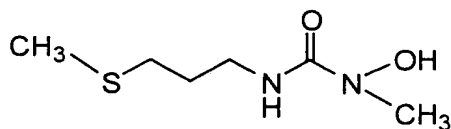
(IX-1-28)



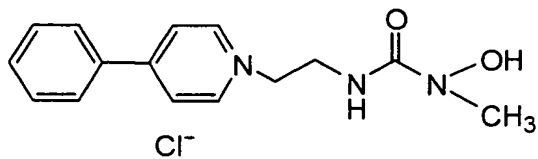
(IX-1-29)



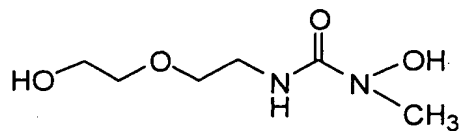
(IX-1-30)



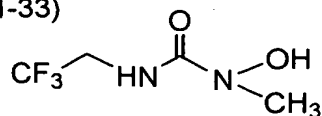
(IX-1-31)



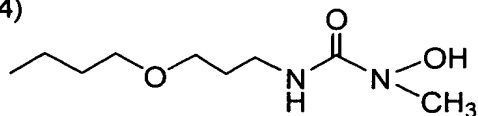
(IX-1-32)



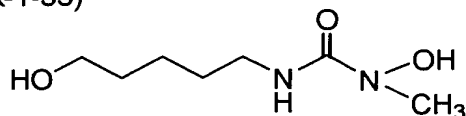
(IX-1-33)



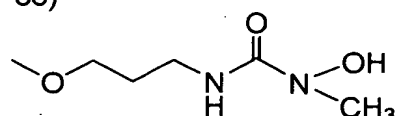
(IX-1-34)



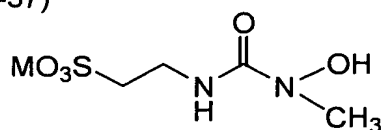
(IX-1-35)



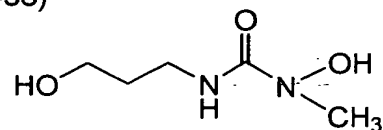
(IX-1-36)



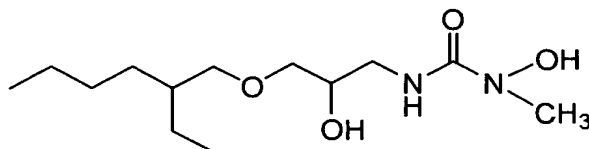
(IX-1-37)



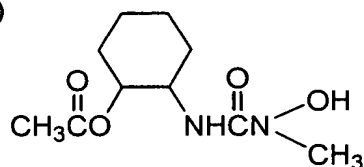
(IX-1-38)



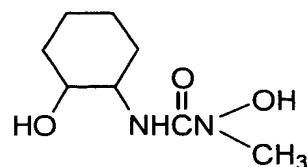
(IX-1-39)



(IX-1-40)



(IX-1-41)



These compounds used in the present invention can be easily prepared by the methods described in J. Org. Chem., 27, 4054 ('62), J. Amer. Chem. Soc., 73, 2981 ('51) and JP-B-49-10692 and methods according to them.

In the present invention, the compound represented by general formula (IX) may be added after being dissolved in any of water, a water-soluble solvent such as methanol and ethanol, and a solvent mixture of these, or by emulsion dispersion. When a compound is dissolved in water, if the compound becomes to exhibit an increased solubility when the pH is raised or lowered, it can be added after being dissolved through

the raising or lowering of the pH. It is also possible to cause a surfactant to coexist.

In the present invention, the compound represented by general formula (IX-1) is preferably added when an emulsion is prepared. When a compound is added in the preparation of an emulsion, this compound can be added at any point during the preparation. For example, the compound can be added during silver halide grain formation, before or during desalting, before or during chemical ripening, or before the preparation of a complete emulsion. The compound can also be added separately a plurality of times during these steps. Preferably, it is added before, during or after chemical sensitization. Further, it may be added before application of a coating solution. It may be added to a layer adjacent to an emulsion layer or another layer, resulting in its addition to the emulsion layer through its diffusion in the layer. Further, it is also possible use a mixture obtained by dispersing and dissolving the compound in an emulsified material after mixing the mixture with the above-mentioned emulsion.

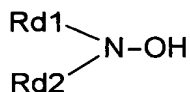
The preferable addition amount of the compound represented by general formula (IX-1) depends greatly on the manner of its addition as described above and the kind of the compound to be added, but the compound is used preferably in an amount of from  $1 \times 10^{-6}$  mol

to  $5 \times 10^{-2}$  mol, more preferably from  $1 \times 10^{-5}$  mol to  $5 \times 10^{-3}$  mol, per mol of an lightsensitive silver halide.

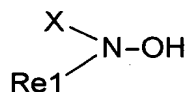
Next, the compound represented by general formula (IX-2) of the present invention will be described in detail.

G1 and G2 each represent a hydrogen atom or a monovalent substituent. They may be bonded together to form a ring. As the monovalent substituent, any one can be applied, but preferred is the aforementioned Yy. Preferred is a compound selected from the following general formulas (A-I), (A-II), (A-III), (A-IV) and (A-V):

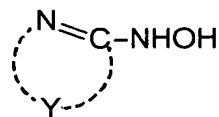
(A-I)



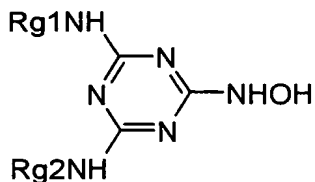
(A-II)



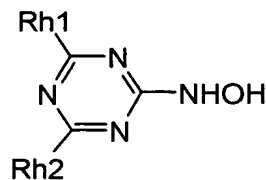
(A-III)



(A-IV)



(A-V)



In general formula (A-I), Rd1 represents an alkyl group, an alkenyl group, an aryl group, an acyl group, an alkyl- or arylsulfonyl group, an alkyl- or arylsulfinyl group, a carbamoyl group, a sulfamoyl group, an alkoxy carbonyl group or an aryloxy carbonyl group. Rd2 represents a hydrogen atom or a group presented for Rd1. It is to be noted that when Rd1 is

an alkyl group, an alkenyl group or an aryl group, Rd2 is an acyl group, an alkyl- or arylsulfonyl group, an alkyl- or arylsulfinyl group, a carbamoyl group, a sulfamoyl group, an alkoxycarbonyl group or an aryloxycarbonyl group. Rd1 and Rd2 may be combined to form a 5- to 7-membered ring. In general formula (A-II), X represents a heterocyclic group, and Rel represents an alkyl group, an alkenyl group or an aryl group. X and Rel may be combined to form a 5- to 7-membered ring. In general formula (A-III), Y represents a group of non-metallic atoms required to form a 5-membered ring together with the -N=C- group. Y further represents a group of nonmetallic atoms required to form a 6-membered ring together with the -N=C- group, and the end of Y at which Y bonds with the carbon atom of the -N=C- group is a group selected from the group consisting of -N(Rf1)-, -C(Rf2)(Rf3)-, -C(Rf4)=, -O- and -S-, each of which bonds with the carbon atom of the -N=C- group via the left side bond thereof, and the above Rf1 to Rf4 each represent a hydrogen atom or a substituent. In general formula (A-IV), Rg1 and Rg2 may be the same or different from each other and each represent an alkyl group or an aryl group, provided that, when both Rg1 and Rg2 are the same substituted alkyl groups, each of Rg1 and Rg2 represents an alkyl group having 8 or more carbon atoms. In general formula (A-V), Rh1 and Rh2 may be the same

or different from each other and each represent a hydroxylamino group, a hydroxyl group, an amino group, an alkylamino group, an arylamino group, an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, an alkyl group or an aryl group, provided that Rh1 and Rh2 do not simultaneously represent -NHRh3, wherein Rh3 represents an alkyl group or an aryl group. Rd1 and Rd2, and X and Rel may be bonded together to form a 5- to 7-membered ring.

The inventors of the present invention have found that oxygen is one of the causes of variations in the photographic properties occurring while a lightsensitive material is stored or after photographing and before development. They estimate that a certain compound in a lightsensitive material reacts with oxygen to have an influence on the photographic properties and compounds represented by formulas (A-I) to (A-V) above capture this compound. Variations of the photographic properties are sometimes increased when a gelatin coating amount is increased. They estimate that this is so because a slight amount of an impurity in gelatin reacts with oxygen to have an influence on the photographic properties. It is also found that the resistance to pressure can be improved by the compounds represented by formulas (A-I) to (A-V). The present invention will be described in more detail below.

The compounds represented by general formulas (A-I) to (A-V) will be described in more detail.

In these formulas, the alkyl group is a straight chain, branched or cyclic alkyl group, which may have a substituent. In general formula (A-I), Rd1 represents an alkyl group (preferably, an alkyl group having 1-36 carbon atoms, e.g., methyl, ethyl, i-propyl, cyclopropyl, butyl, isobutyl, cyclohexyl, t-octyl, decyl, dodecyl, hexadecyl and benzyl), an alkenyl group (preferably, an alkenyl group having 2-36 carbon atoms, e.g., allyl, 2-butenyl, isopropenyl, oleyl and vinyl), an aryl group (preferably, an aryl group having 6-40 carbon atoms, e.g., phenyl and naphthyl), an acyl group (preferably, an acyl group having 2-36 carbon atoms, e.g., acetyl, benzoyl, pivaloyl,  $\alpha$ -(2,4-di-tert-amylphenoxy)butyryl, myristoyl, stearoyl, naphthoyl, m-pentadecylbenzoyl, and isonicotinoyl), an alkyl- or arylsulfonyl group (preferably, an alkylsulfonyl group having 1-36 carbon atoms or an arylsulfonyl group having 6-36 carbon atoms, e.g., methanesulfonyl, octanesulfonyl, benzenesulfonyl and toluenesulfonyl), an alkyl- or arylsulfinyl group (preferably an alkylsulfinyl group having 1-40 carbon atoms or an arylsulfinyl group having 6-40 carbon atoms, e.g., methanesulfinyl and benzenesulfinyl), a carbamoyl group (also including an N-substituted carbamoyl group and preferably a carbamoyl group having 0-40 carbon atoms,

e.g., N-ethylcarbamoyl, N-phenylcarbamoyl, N,N-dimethylcarbamoyl and N-butyl-N-phenylcarbamoyl), a sulfamoyl group (also including an N-substituted sulfamoyl group and preferably a sulfamoyl group having 1-40 carbon atoms, e.g., N-methylsulfamoyl, N,N-diethylsulfamoyl, N-phenylsulfamoyl, N-cyclohexyl-N-phenylsulfamoyl and N-ethyl-N-dodecylsulfamoyl), an alkoxycarbonyl group (preferably an alkoxycarbonyl group having 2-36 carbon atoms, e.g., methoxycarbonyl, cyclohexyloxycarbonyl, benzyloxycarbonyl, isoamyloxycarbonyl and hexadecyloxycarbonyl), or an aryloxycarbonyl group (preferably an aryloxycarbonyl group having 7 to 40 carbon atoms, e.g., phenoxycarbonyl and naphthoxycarbonyl). Rd2 represents a hydrogen atom or a group presented for Rd1.

In general formula (A-II), X represents a heterocyclic group (a group which forms a 5- to 7-membered heterocyclic ring having at least one of a nitrogen atom, a sulfur atom, an oxygen atom and a phosphor atom as a ring constituent atom and in which the bonding position (the position of a monovalent group) of the heterocyclic ring is preferably a carbon atom, e.g., 1,3,5-triazin-2-yl, 1,2,4-triazin-3-yl, pyridin-2-yl, pyradinyl, pyrimidinyl, purinyl, quinolyl, imidazolyl, 1,2,4-triazol-3-yl, benzimidazol-2-yl, thienyl, furyl, imidazolydiny, pyrrolinyl, tetrahydrofuryl, morpholinyl and phosphinolin-2-yl).



Rel represents an alkyl group, an alkenyl group or an aryl group in the same meaning as Rdl in general formula (A-I).

5 In formula (A-III), Y represents a group of non-metallic atoms (e.g., the cyclic group formed is imidazolyl, benzimidazolyl, 1,3-thiazol-2-yl, 2-imidazolin-2-yl, purinyl or 3H-indol-2-yl) required to form a 5-membered ring together with  $-N=C-$ . Y further represents a group of non-metallic atoms required to  
10 form a 6-membered ring together with the  $-N=C-$  group, and the end of Y which bonds to a carbon atom in the  $-N=C-$  group represents a group (which bonds to a carbon atom in  $-N=C-$  on the left side of the group) selected from  $-N(Rf1)-$ ,  $-C(Rf2)(Rf3)-$ ,  $-C(Rf4)=$ ,  $-O-$ , and  $-S-$ .  
15 Rf1 to Rf4 may be the same or different and each represents a hydrogen atom or a substituent (e.g., an alkyl group, an alkenyl group, an aryl group, an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, an alkylamino group, an arylamino group  
20 and a halogen atom). Examples of the 6-membered cyclic group formed by Y are quinolyl, isoquinolyl, phthaladiny, quinoxaliny, 1,3,5-triazin-5-yl and 6H-1,2,5-thiadiazin-6-yl.

In general formula (A-IV), each of Rg1 and Rg2  
25 represents an alkyl group (preferably an alkyl group having 1-36 carbon atoms, e.g., methyl, ethyl, i-propyl, cyclopropyl, n-butyl, isobutyl, hexyl, cyclohexyl, t-

octyl, decyl, dodecyl, hexadecyl and benzyl) or an aryl group (preferably an aryl group having 6-40 carbon atoms, e.g., phenyl and naphthyl). When Rg1 and Rg2 are simultaneously unsubstituted alkyl groups and Rg1 and Rg2 are identical groups, Rg1 and Rg2 are alkyl groups having 8 or more carbon atoms.

In general formula (A-V), each of Rh1 and Rh2 represents a hydroxylamino group, a hydroxyl group, an amino group, an alkylamino group (preferably an alkylamino group having 1-50 carbon atoms, e.g., methylamino, ethylamino, diethylamino, methylethylamino, propylamino, dibutylamino, cyclohexylamino, t-octylamino, dodecylamino, hexadecylamino, benzylamino and benzylbutylamino), an arylamino group (preferably an arylamino group having 6-50 carbon atoms, e.g., phenylamino, phenylmethylamino, diphenylamino and naphthylamino), an alkoxy group (preferably an alkoxy group having 1-36 carbon atoms, e.g., methoxy, ethoxy, butoxy, t-butoxy, cyclohexyloxy, benzyloxy, octyloxy, tridecyloxy and hexadecyloxy), an aryloxy group (preferably an aryloxy group having 6-40 carbon atoms, e.g., phenoxy and naphthoxy), an alkylthio group (preferably an alkylthio group having 1-36 carbon atoms, e.g., methylthio, ethylthio, i-propylthio, butylthio, cyclohexylthio, benzylthio, t-octylthio and dodecylthio), an arylthio group (preferably an arylthio group having 6-40 carbon atoms, e.g., phenylthio and

naphthylthio), an alkyl group (preferably an alkyl group having 1-36 carbon atoms, e.g., methyl, ethyl, propyl, butyl, cyclohexyl, i-amyl, sec-hexyl, t-octyl, dodecyl and hexadecyl), or an aryl group (preferably an aryl group having 6-40 carbon atoms, e.g., phenyl and naphthyl). It is to be noted that Rh1 and Rh2 cannot be -NHR (R is an alkyl group or an aryl group) at the same time.

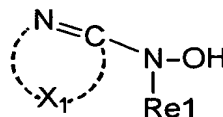
Rd1 and Rd2 or X and Re1 may be bonded together to form a 5- to 7-membered ring. Examples of such a ring include a succinimide ring, a phthalimide ring, a triazole ring, a urazol ring, a hydantoin ring and a 2-oxo-4-oxazolidinone ring. Each group in the compounds represented by general formulas (A-I) to (A-V) may be further substituted with a substituent. Examples of such a substituent include an alkyl group, an alkenyl group, an aryl group, a heterocyclic group, a hydroxyl group, an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, an amino group, an acylamino group, a sulfonamide group, an alkylamino group, an arylamino group, a carbamoyl group, a sulfamoyl group, a sulfo group, a carboxyl group, a halogen atom, a cyano group, a nitro group, a sulfonyl group, an acyl group, an alkoxycarbonyl group, an aryloxycarbonyl group, an acyloxy group and a hydroxyamino group.

In general formula (A-I), preferred is a compound in which Rd2 is a hydrogen atom, an alkyl group, an

alkenyl group or an aryl group and Rd1 is an acyl group,  
a sulfonyl group, a sulfinyl group, a carbamoyl group,  
a sulfamoyl group, an alkoxycarbonyl group or an  
aryloxycarbonyl group. More preferred is a compound in  
5 which Rd2 is an alkyl group or an alkenyl group and Rd1  
is an acyl group, a sulfonyl group, a carbamoyl group,  
a sulfamoyl group, an alkoxycarbonyl group or an  
aryloxycarbonyl group. The most preferred is a  
compound in which Rd2 is an alkyl group and Rd1 is an  
10 acyl group.

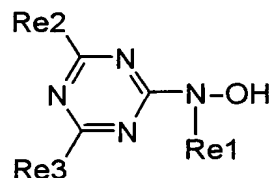
In general formula (A-II), Re1 is an alkyl group  
or an alkenyl group is preferable. A compound in which  
Re1 is an alkyl group is more preferable. On the other  
hand, as general formula (A-II), a compound represented  
15 by the following general formula (A-II-1) is preferable,  
and it is more preferable that X is 1,3,5-triazin-2-yl.  
A compound represented by the following general formula  
(A-II-2) is most preferable.

(A-II-1)



20 In general formula (A-II-1), Re1 represents Re1 in  
general formula (A-II), and X<sub>1</sub> represents a group of  
non-metallic atoms required to form a 5- or 6-membered  
ring. Of the compounds represented by general formula  
(A-II-1), a compound in which X<sub>1</sub> forms a 5- or 6-  
25 membered heterocyclic aromatic ring is more preferable.

(A-II-2)



In general formula (A-II-2), Re1 has the same meaning as Re1 in general formula (A-II). Re2 and Re3 may be the same or different and each represent a hydrogen atom or a substituent. Of the compounds represented by general formula (A-II-2), a compound in which each of Re2 and Re3 is a hydroxyamino group, a hydroxyl group, an amino group, an alkylamino group, an arylamino group, an alkoxy group, an aryloxy group, an alkylthio group, an arylthio group, an alkyl group or an aryl group is particularly preferable.

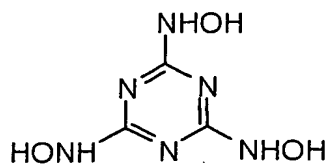
Of the compounds represented by general formula (A-III), a compound in which Y is a group of non-metal atoms required to form a 5-membered ring is preferable, and a compound in which the end atom of Y which bonds to a carbon atom of the  $-N=C-$  group is a nitrogen atom is more preferable. A compound in which Y forms an imidazoline ring is most preferable. This imidazoline ring may also be condensed with a benzene ring.

Of the compounds represented by general formula (A-IV), a compound in which each of Rg1 and Rg2 is an alkyl group is preferable. In general formula (A-V), each of Rh1 and Rh2 is preferably a group selected from a hydroxyamino group, an alkylamino group and an alkoxy group. It is particularly preferable that Rh1 is a

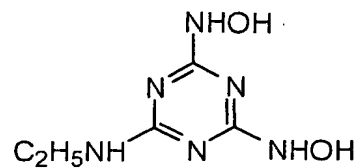
hydroxylamino group and Rh2 is an alkylamino group.

Of the compounds represented by general formulas (A-I) to (A-V), a compound having 15 or less carbon atoms in total is preferable to be made act also on layers other than the layer to which it is added, and a compound having 16 or more carbon atoms in total is preferable to be made act only on the layer to which it is added. Of the compounds represented by general formulas (A-I) to (A-V), the compounds represented by general formulas (A-I), (A-II), (A-IV) and (A-V) are preferable, the compounds represented by general formulas (A-I), (A-IV) and (A-V) are more preferable, and the compounds represented by general formulas (A-I) and (A-V) are most preferable. Specific examples of the compounds represented by general formulas (A-I) to (A-V) are presented below, but the present invention is not restricted to them.

IX-2-1



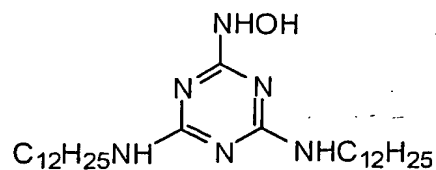
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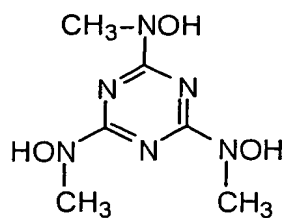
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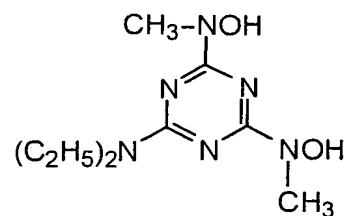
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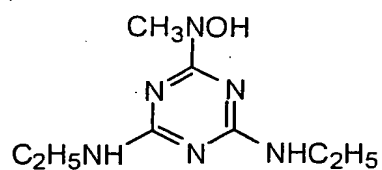
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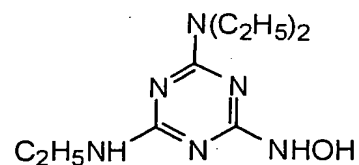
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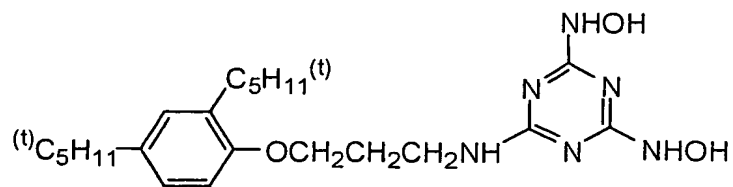
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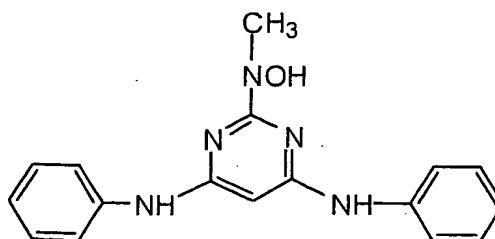
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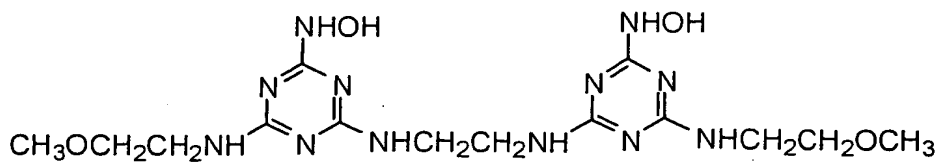
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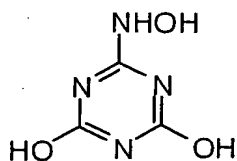
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IX-2-11



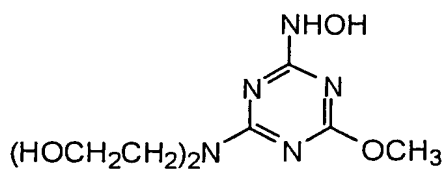
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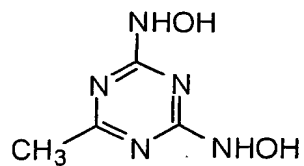
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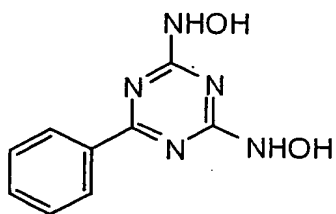
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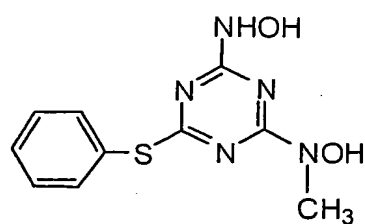
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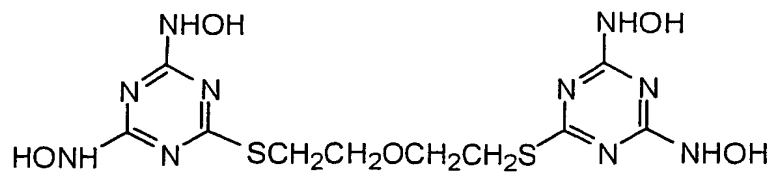
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IX-2-17

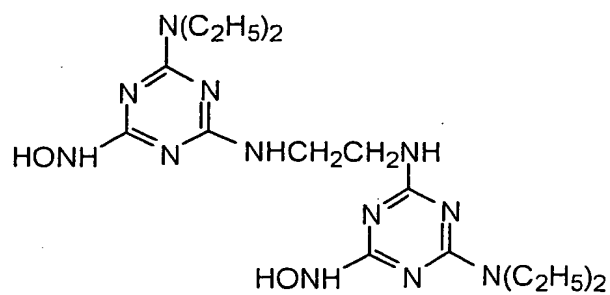


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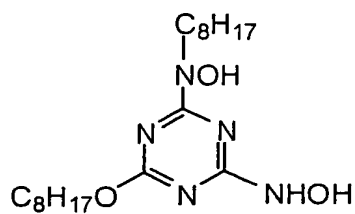




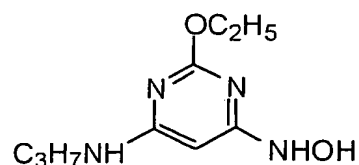
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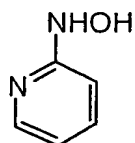
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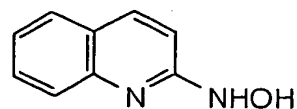
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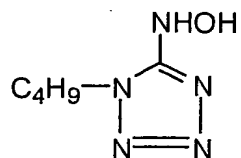
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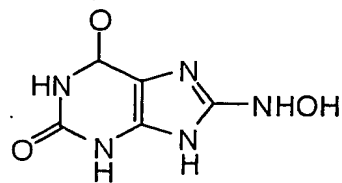
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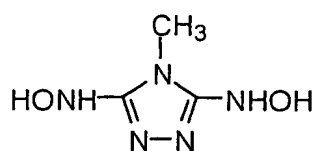
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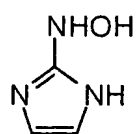
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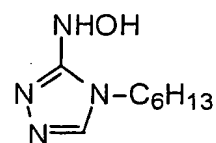
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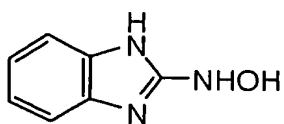
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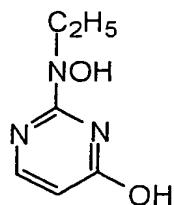
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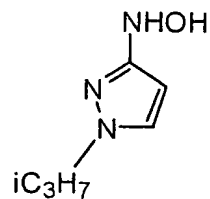
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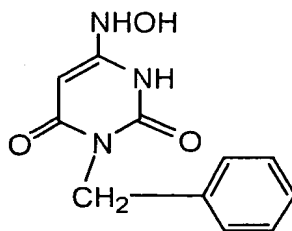
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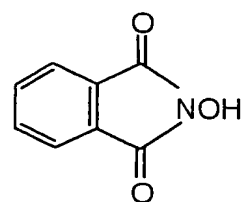
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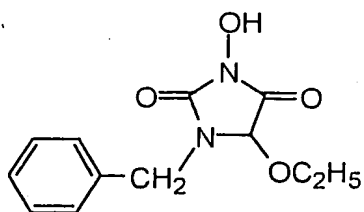
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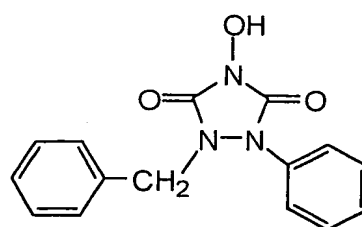
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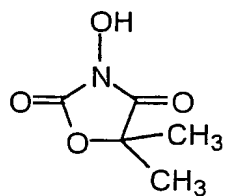
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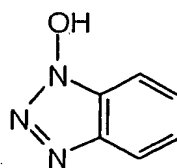
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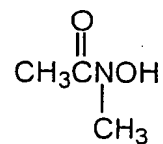
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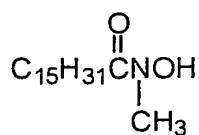
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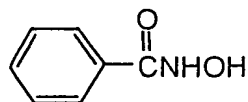
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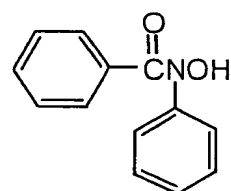
IX-2-39



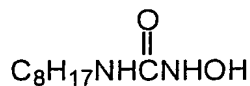
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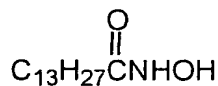
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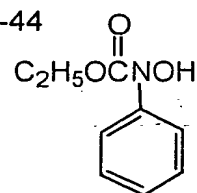
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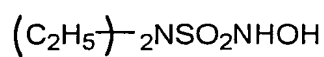
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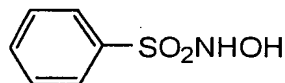
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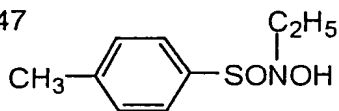
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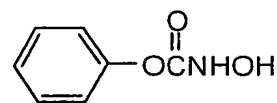
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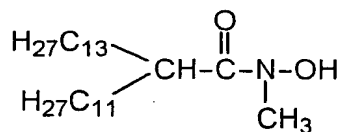
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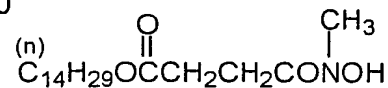
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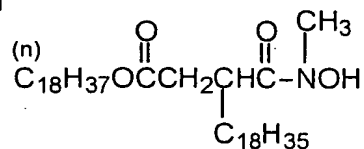
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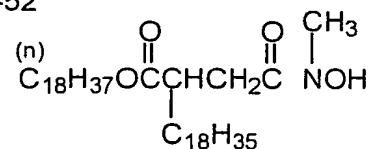
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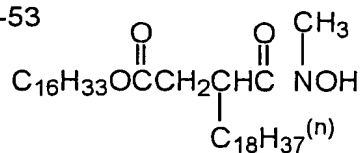
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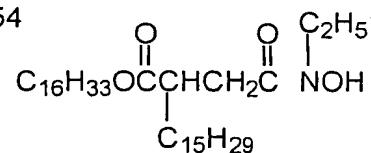
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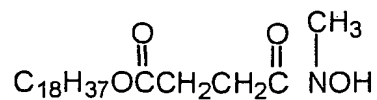
IX-2-53



IX-2-54



IX-2-55



The correspondence between these compounds and general formulas (A-I) to (A-V) is as follows:

General formula (A-I): A-33 to A-55.

General formula (A-II): A-5 to A-7, A-10, A-20, A-

5 30.

General formula (A-III): A-21 to A-29, A-31, A-32.

General formula (A-IV): A-8, A-11, A-19.

General formula (A-V): A-1 to A-4, A-9, A-12 to A-

18

10        These compounds of the present invention can be easily synthesized by methods described in, for example, J. Org. Chem., 27, 4054 ('62), J. Amer. Chem. Soc., 73, 2981 ('51), and JP-B-49-10692, or by methods based on these methods. In the present invention, the compounds  
15        represented by general formulas (A-I) to (A-V) may be added after being dissolved in any of water, a water-soluble solvent such as methanol or ethanol, and a solvent mixture of these solvents, or may be added by emulsion dispersion. Further, they may also be added  
20        prior to the preparation of an emulsion. When a compound is dissolved in water, if the compound becomes to exhibit an increased solubility when the pH is raised or lowered, it may be added after being dissolved through the raising or lowering of the pH.  
25        In the present invention, two or more different types of the compounds represented by general formulas (A-I) to (A-V) may be used together. For example, using a

water soluble compound and an oil soluble compound in combination is advantageous from the viewpoint of photographic performance. The application amounts of the compounds (A-I) to (A-V) are preferably  $10^{-4}$  mmol/m<sup>2</sup> to 10 mmol/m<sup>2</sup>, and more preferably  $10^{-3}$  mmol/m<sup>2</sup> to 1 mmol/m<sup>2</sup>.

Next, the compound represented by general formula (X) will be described. In general formula (X), Rb17, Rb18 and Rb19 each independently represent a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group, an aryl group or a heterocyclic group. Rb20 represents a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group, an aryl group, a heterocyclic group or NRb21Rb22. J represents -CO- or -SO<sub>2</sub>-, and n represents 0 or 1. Rb21 represents a hydrogen atom, a hydroxyl group, an amino group, an alkyl group, an alkenyl group, an alkynyl group, an aryl group or a heterocyclic group. Rb22 represents a hydrogen atom, an alkyl group, an alkenyl group, an alkynyl group, an aryl group or a heterocyclic group.

In Rb17, Rb18 and Rb19, the alkyl group, the alkenyl group and the alkynyl group are those having 1-30 carbon atoms, and particularly a straight chain, branched or cyclic alkyl having 1-10 carbon atoms, an alkenyl group having 2-10 carbon atoms and an alkynyl group having 2-10 carbon atoms. Examples of the alkyl group, the alkenyl group, the alkynyl group and the

aralkyl group include methyl, ethyl, propyl, cyclopropyl, allyl, propargyl and benzyl. In Rb17, Rb18 and Rb19, the aryl group is preferably an aryl group having 6-30 carbon atoms, and particularly preferably, a monocyclic or condensed aryl group having 6-12 carbon atoms. Examples thereof are phenyl and naphthyl. In Rb17, Rb18 and Rb19, the heterocyclic group represented is a 3- to 10-membered, saturated or unsaturated, heterocyclic group containing at least one of a nitrogen atom, oxygen atom and sulfur atom. This group may be a monocyclic ring or may form a condensed ring with another aromatic ring. The heterocycle is preferably a 5- or 6-membered, aromatic, heterocyclic ring. Examples thereof include pyridyl, imidazolyl, quinolyl, benzimidazolyl, pyrimidyl, pyrazolyl, isoquinolyl, thiazolyl, thienyl, furyl and benzothioazolyl.

In Rb20, the alkyl group, the alkenyl group, the alkynyl group, the aryl group and the heterocyclic group have the same meanings as Rb17, Rb18 and Rb19. In NRb21Rb22 of Rb20, the alkyl group, the alkenyl group, the alkynyl group, the aryl group and the heterocyclic group have the same meanings as Rb17, Rb18 and Rb19. Each of the substituents represented by Rb17, Rb18, Rb19, Rb20, Rb21 and Rb22 may be substituted with the aforementioned substituent Yy.

In general formula (X), Rb17 and Rb18, Rb17 and

Rb19, Rb19 and Rb20, or Rb20 and Rb18 may be bonded together to form a ring.

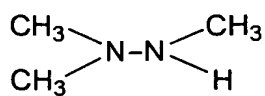
In general formula (X), when n is 0, it is preferable that Rb17, Rb18 and Rb19 are each an alkyl group having 1-10 carbon atoms, an alkenyl group having 2-10 carbon atoms, an alkynyl group having 2-10 carbon atoms, an aryl group having 6-10 carbon atoms or a nitrogen-containing heterocyclic group, Rb20 is a hydrogen atom, an alkyl group having 1-10 carbon atoms, an alkenyl group having 2-10 carbon atoms, an alkynyl group having 2-10 carbon atoms, an aryl group having 6-10 carbon atoms, or a nitrogen-containing heterocyclic group. It is more preferable that Rb17, Rb18 and Rb19 are each an alkyl group having 1-10 carbon atoms, an alkenyl group having 2-10 carbon atoms, an alkynyl group having 2-10 carbon atoms, an aryl group having 6-10 carbon atoms or a nitrogen-containing heterocyclic group, Rb20 is a hydrogen atom. When n is 1, it is preferable that Rb17, Rb18 and Rb19 are each a hydrogen atom, an alkyl group having 1-10 carbon atoms, an alkenyl group having 2-10 carbon atoms, an alkynyl group having 2-10 carbon atoms, an aryl group having 6-10 carbon atoms or a nitrogen-containing heterocyclic group, J is -CO-, Rb20 is a hydrogen atom, an alkyl group having 1-10 carbon atoms, an alkenyl group having 2-10 carbon atoms, an alkynyl group having 2-10 carbon atoms, an aryl group having 6-10 carbon atoms, a

nitrogen-containing heterocyclic group or NRb21Rb22,  
Rb21 is a hydrogen atom, a hydroxyl group, an amino  
group, an alkyl group having 1-10 carbon atoms, an  
alkenyl group having 2-10 carbon atoms, an alkynyl  
5 group having 2-10 carbon atoms, an aryl group having 6-  
10 carbon atoms or a nitrogen-containing heterocyclic  
group, and Rb22 is a hydrogen atom, an alkyl group  
having 1-10 carbon atoms, an alkenyl group having 2-10  
carbon atoms, an alkynyl group, an aryl group having 6-  
10 carbon atoms or a nitrogen-containing heterocyclic  
group. It is more preferable that Rb17 is an aryl  
group having 6-10 carbon atoms, Rb18 and Rb19 are each  
a hydrogen atom, J is -CO-, Rb20 is NRb21Rb22, and Rb59  
is a hydrogen atom, a hydroxyl group, an alkyl group  
15 having 1-10 carbon atoms, an alkenyl group or an  
alkynyl group.

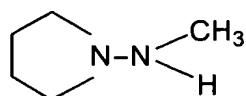
Specific examples of the compound represented by  
general formula (X) are presented below, but the  
present invention is not restricted to them.



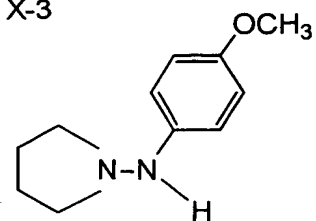
X-1



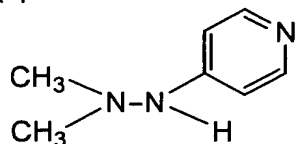
X-2



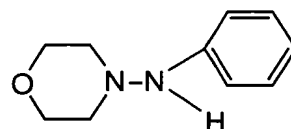
X-3



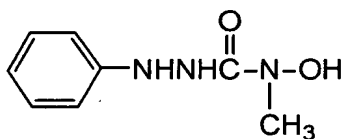
X-4



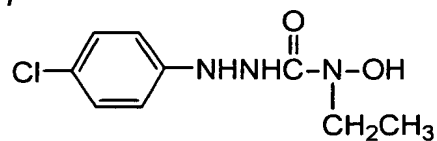
X-5



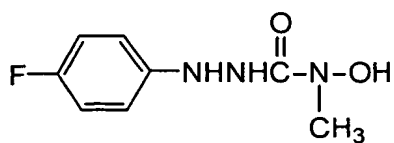
X-6



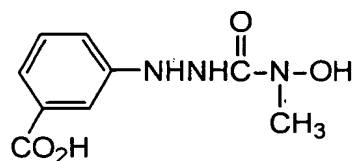
X-7



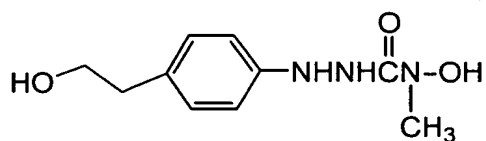
X-8



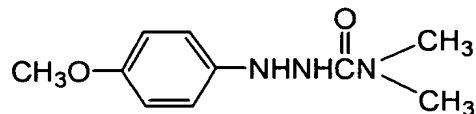
X-9



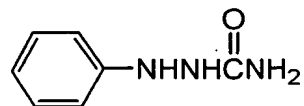
X-10



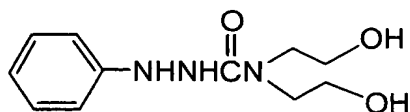
X-11



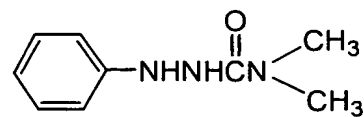
X-12



X-13



X-14



The compound represented by general formula (X) is readily available as chemicals on the market or as a compound synthesized from these chemicals on the market by known methods.

5           The compound represented by general formula (X) is preferably added to a layer adjacent to an emulsion layer or another layer before or during application of a coating solution, thereby being added to the emulsion layer through its dispersion therein. It is also  
10 possible to add that compound before, during or after the chemical sensitization in preparation of an emulsion. The preferable addition amount of that compound depends greatly on the manner of its addition as described above and the kind of the compound to be  
15 added, but in general, the compound is used in an amount of from  $5 \times 10^{-6}$  mol to 0.05 mol, preferably from  $1 \times 10^{-5}$  mol to 0.005 mol, per mol of an lightsensitive silver halide. The addition of the compound in an amount more than the amount mentioned  
20 above is not preferable because it will result in some adverse effect such as increase of fogging. It is preferable that the compound represented by general formula (X) is added after being dissolved in a water-soluble solvent. The pH of the solution may be  
25 decreased or increased with an acid or a base, and a surfactant may exist together with that compound. Further, that compound may be added after being formed

into an emulsified dispersion and then being dissolved in a high boiling organic solvent. Alternatively, it may be added after being formed into a fine crystal dispersion by a known dispersing process. Two or more compounds represented by general formula (X) may be used together. When two or more compounds are used together, they may be added to either the same layer or separate layers.

Here, the above general formula (XI) will be described in more detail.

In the general formula (XI),  $X^2$  and  $Y^2$  each independently represent a hydroxyl group,  $-NR^{i23}R^{i24}$  or  $-NHSO_2R^{i25}$ .  $R^{i21}$  and  $R^{i22}$  each independently represent a hydrogen atom or an optional substituent. Examples of such an optional substituent include an alkyl group (preferably that having 1-20 carbon atoms, e.g., methyl, ethyl, octyl, hexadecyl and t-butyl), an aryl group (preferably that having 6-20 carbon atoms, e.g., phenyl and p-tolyl), an amino group (preferably that having 0-20 carbon atoms, e.g., unsubstituted amino, diethylamino, diphenylamino and hexadecylamino), an amide group (preferably that having 1-20 carbon atoms, e.g., acetylamino, benzoylamino, octadecanoylamino and benzenesulfonamind), an alkoxy group (preferably that having 1-20 carbon atoms, e.g., methoxy, ethoxy and hexadecyloxy), an alkylthio group (preferably that 1-20 carbon atoms, e.g., methylthio, butylthio and

octadecylthio), an acyl group (preferably that having  
1-20 carbon atoms, e.g., acetyl, hexadecanoyl, benzoyl  
and benzenesulfonyl), a carbamoyl group (preferably  
that having 1-20 carbon atoms, e.g., unsubstituted  
5 carbamoyl, N-hexylcarbamoyl and N,N-diphenylcarbamoyl),  
an alkoxy carbonyl group (preferably that having 2-20  
carbon atoms, e.g., methoxycarbonyl and  
octyloxycarbonyl), a hydroxyl group, a halogen atom  
(e.g., F, Cl and Br), a cyano group, a nitro group, a  
10 sulfo group and a carboxyl group.

These substituents may further be substituted with  
another substituent (e.g., those presented for Yy).

Ri21 and Ri22 may be bonded together to form a  
carbon ring or a heterocycle (both preferably being a  
15 5- to 7-membered ring). Ri23 and Ri24 each  
independently represent a hydrogen atom, an alkyl group  
(preferably that having 1-10 carbon atoms, e.g., ethyl,  
hydroxyethyl and octyl), an aryl group (preferably that  
having 6-10 carbon atoms, e.g., phenyl and naphthyl),  
20 or a heterocyclic group (preferably that having 2-10  
carbon atoms, e.g., 2-furanyl and 4-pyridyl), and these  
may further be substituted with a substituent.

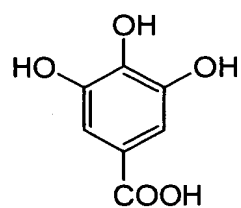
Ri23 and Ri24 may be bonded together to form a  
nitrogen-containing heterocycle (preferably a 5- to 7-  
25 membered ring). Ri25 represents an alkyl group  
(preferably that having 1-20 carbon atoms, e.g., ethyl,  
octyl and hexadecyl), an aryl group (preferably that

having 6-20 carbon atoms, e.g., phenyl, p-tolyl and 4-dodecyloxyphenyl), an amino group (preferably that having 0-20 carbon atoms, e.g., N,N-diethylamino, N,N-diphenylamino and morpholino), or a heterocyclic group (preferably that having 2-20 carbon atoms, e.g., 3-pyridyl), and these may further be substituted.

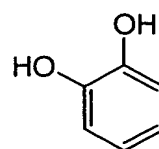
In general formula (XI),  $X^2$  is preferably -NR<sup>i23</sup>R<sup>i24</sup> or -NHSO<sub>2</sub>R<sup>i25</sup>. R<sup>i21</sup> and R<sup>i22</sup> are each preferably a hydrogen atom, an alkyl group or an aryl group. They may be bonded together to form a carbon ring or a heterocycle. Details of these groups are the same as R<sup>i23</sup> and R<sup>i24</sup>.

Specific examples of the compound represented by general formula (XI) are presented below, but the present invention is not restricted to them.

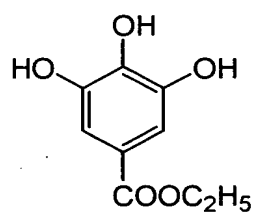
XI-1



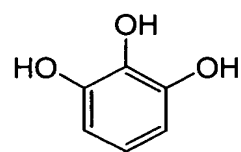
XI-6



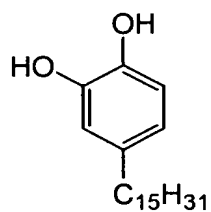
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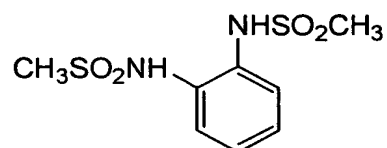
XI-7



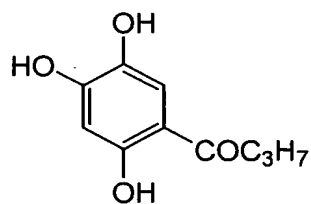
XI-3



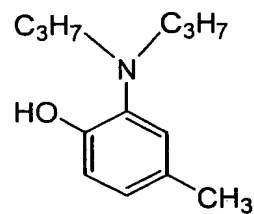
XI-8



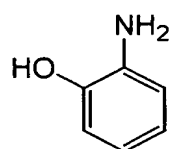
XI-4



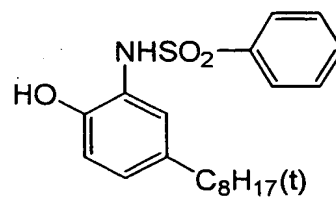
XI-9

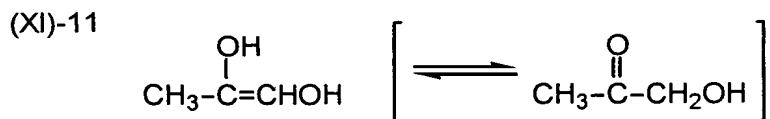


XI-5

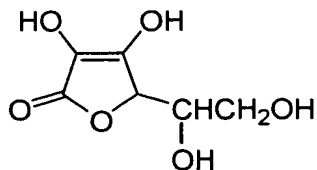


XI-10

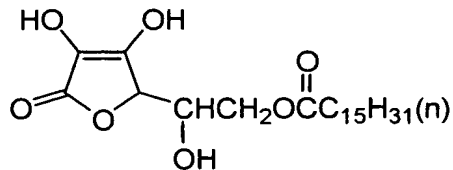




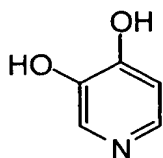
(XI)-12



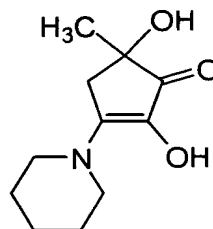
(XI)-13



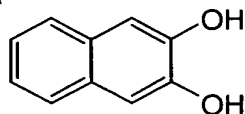
(XI)-14



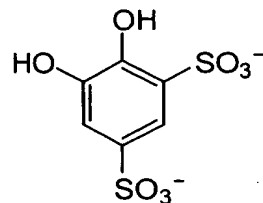
(XI)-16



(XI)-15



(XI)-17



Among the compounds represented by formulas (VI) to (XI), those represented by formulas (IX-1), (IX-2), (VIII-1), (VII-2), (VII), (VI), and (X) are preferable, those represented by (IX-1), (IX-2), (VIII-1), (VII-2), and (VII) are more preferable, and those represented by formulas (IX-1), (IX-2), (VIII-1), and (VIII-2) are much more preferable. Especially preferable compounds are those represented by formulas (IX-1) and (IX-2).

With respect to the lightsensitive layer of the

present invention, one or more layers may be provided on a support. The layers may be provided not only on one side of the support but also on both sides thereof. The lightsensitive layer of the present invention may  
5 be used for black-and-white silver halide photographic lightsensitive materials (e.g., X-ray lightsensitive materials, lithographic lightsensitive materials and negative films for black-and-white photographing) and color photographic lightsensitive materials (e.g.,  
10 color negative films, color reversal films and color papers). In addition, the lightsensitive layer of the present invention may also be used for diffusion transfer lightsensitive materials (e.g., color  
diffusion transfer elements and silver salt diffusion  
15 transfer elements), and heat-developable lightsensitive materials (both black-and-white and color).

The color photographic lightsensitive material will be described in detail below, but it is not limited to this description.

20 The silver halide photographic material is only required to be provided with at least one of a blue-sensitive layer, a green-sensitive layer and a red-sensitive layer, on a support. The number of layers and order thereof of the material is not particularly  
25 limited. As an typical example, a silver halide photographic lightsensitive material provided with at least one unit of silver halide emulsion layers each



having the same color-sensitivity but different in light-sensitivity, on a support, can be mentioned. The silver halide emulsion layers are a unit lightsensitive layer sensitive to one of blue light, green light and red light. In a multi-layered silver halide color photographic material, the unit lightsensitive layers are usually arranged in an order of a red-sensitive layer, a green-sensitive-layer, and a blue-sensitive layer on a support in this order from the one closest to the support. However, the arrangement order may be reversed depending on the purpose of the photographic material. Further, the arrangement order in which a different lightsensitive layer is sandwiched between the same color sensitive layers may be acceptable.

A non lightsensitive layer, such as a inter layer for each layer, can be formed between the silver halide lightsensitive layers and as the uppermost layer and the lowermost layer.

These intermediate layers may contain couplers and DIR compounds described in JP-A's-61-43748, 59-113438, 59-113440, 61-20037 and 61-20038, and may contain color-mixing inhibitor as usually may be.

As for a plurality of silver halide emulsion layers constituting respective unit lightsensitive layer, a two-layered structure of high- and low-speed emulsion layers can be preferably used as described in DE (German Patent) 1,121,470 or GB 923,045, the

disclosures of which are incorporated herein by  
reference. Usually, preferable arrangement of high-  
and low-speed emulsion layers is in this order so as to  
the speed becomes lower toward the support, and a non  
5 lightsensitive layer may be arranged between each  
silver halide emulsion layers. Also, as described in  
JP-A's-57-112751, 62-200350, 62-206541 and 62-206543,  
the disclosures of which are incorporated herein by  
reference, layers can be arranged such that a low-speed  
10 emulsion layer is formed farther from a support and a  
high-speed layer is formed closer to the support.

More specifically, layers can be arranged from the  
farthest side from a support in the order of low-speed  
blue-sensitive layer (BL)/high-speed blue-sensitive  
15 layer (BH)/high-speed green-sensitive layer  
(GH)/low-speed green-sensitive layer (GL)/high-speed  
red-sensitive layer (RH)/low-speed red-sensitive layer  
(RL), the order of BH/BL/GL/GH/RH/RL or the order of  
BH/BL/GH/GL/RL/RH.

20 In addition, as described in JP-B-55-34932, the  
disclosure of which is incorporated herein by  
reference, layers can be arranged from the farthest  
side from a support in the order of blue-sensitive  
layer/GH/RH/GL/RL. Furthermore, as described in  
25 JP-A's-56-25738 and 62-63936, the disclosures of which  
are incorporated herein by reference, layers can be  
arranged from the farthest side from a support in the

order of blue-sensitive layer/GL/RL/GH/RH.

As described in JP-B-49-15495, the disclosure of which is incorporated herein by reference, three layers can be arranged such that a silver halide emulsion layer having the highest sensitivity is arranged as an upper layer, a silver halide emulsion layer having sensitivity lower than that of the upper layer is arranged as an interlayer, and a silver halide emulsion layer having sensitivity lower than that of the interlayer is arranged as a lower layer; i.e., three layers having different sensitivities can be arranged such that the sensitivity is sequentially decreased toward the support. Even when a layer structure is constituted by three layers having different sensitivities, these layers can be arranged in the order of medium-speed emulsion layer/high-speed emulsion layer/low-speed emulsion layer from the farthest side from a support in a layer sensitive to one color as described in JP-A-59-202464, the disclosure of which is incorporated herein by reference.

In addition, the order of high-speed emulsion layer/low-speed emulsion layer/medium-speed emulsion layer or low-speed emulsion layer/medium-speed emulsion layer/high-speed emulsion layer can be adopted. Furthermore, the arrangement can be changed as described above even when four or more layers are formed.

Various layer configurations and arrangements can be selected depending on the purpose of each lightsensitive material, as mentioned above.

The above various additives can be used in the lightsensitive material according to the present technology, to which other various additives can also be added in conformity with the object.

These additives are described in detail in Research Disclosure Item 17643 (December 1978), Item 18716 (November 1979) and Item 308119 (December 1989), the disclosures of which are incorporated herein by reference. A summary of the locations where they are described will be listed in the following table.

15	Types of additives	RD17643	RD18716	RD308119
	1 Chemical -sensitizers	page 23	page 648 right column	page 996
20	2 Sensitivity increasing agents		page 648 right column	
25	3 Spectral sensitizers, super-sensitizers	pages 23 - 24	page 648, right column to page 649, right column	page 996, right column to page 998, right column
30	4 Brighteners	page 24		page 998 right column
35	5 Antifoggants, and stabilizers	pages 24 - 25	page 649 right column	page 998, right column to page 1000, right column

5	6	Light absorbents, filter dyes, ultraviolet absorbents	pages 25 - 26	page 649, right column to page 650, left column	page 1003, left column to page 1003, right column
10	7	Stain preventing agents	page 25, right column	page 650, left to right columns	page 1002, right column
	8	Dye image stabilizers	page 25		page 1002, right column
15	9	Film hardeners	page 26	page 651, left column	page 1004, right column to page 1005, left column
20	10	Binders	page 26	page 651, left column	page 1003, right column to page 1004, right column
25	11	Plasticizers, lubricants	page 27	page 650, right column	page 1006, left to right columns
30	12	Coating aids, surfactants	pages 26 - 27	page 650, right column	page 1005, left column to page 1006, left column
35	13	Antistatic agents	page 27	page 650, right column	page 1006, right column to page 1007, left column
40	14	Matting agents			page 1008, left column to page 1009, left column

In order to inhibit deterioration in photographic properties due to formaldehyde gas, a compound capable of reacting with and solidifying formaldehyde as disclosed in U.S.P. Nos. 4,411,987 and 4,435,503 can be incorporated in the light-sensitive material.

Various color couples may be used in the present

invention, and the specific examples thereof are described in the patents described in the patents described in the aforementioned Research Disclosure No. 17643, VII-C to G and No. 307105, VII-C to G.

5 Preferred yellow couplers are those described in, for example, U.S.P. Nos. 3,933,051, 4,022,620, 4,326,024, 4,401,752 and 4,248,961, JP-B-58-10739, British Patent Nos. 1,425,020 and 1,476,760, U.S.P. Nos. 3,973,968, 4,314,023 and 4,511,649, and European  
10 Patent No. 249,473A.

Particularly preferred magenta couplers are 5-pyrazolone and pyrazoloazole compounds. Particularly preferred are those described in U.S.P. Nos. 4,310,619 and 4,351,897, European Patent No. 73,636, U.S.P.  
15 Nos. 3,061,432 and 3,725,067, Research Disclosure No. 24220 (June, 1984), JP-A-60-33552, Research Disclosure No. 24230 (June, 1984), JP-A's-60-43659, 61-72238, 60-35730, 55-118034 and 60-185951, U.S.P. Nos. 4,500,630, 4,540,654 and 4,556,630, and  
20 International Publication No. WO 88/04795.

The cyan couplers usable in the present invention are phenolic and naphtholic couplers. Particularly preferred are those described in U.S.P. Nos. 4,052,212, 4,146,396, 4,228,233, 4,296,200, 2,369,929, 2,801,171,  
25 2,772,162, 2,895,826, 3,772,002, 3,758,308, 4,334,011 and 4,327,173, West German Patent Unexamined Published Application No. 3,329,729, European Patent

Nos. 121,365A and 249,453A, U.S.P. Nos. 3,446,622, 4,333,999, 4,775,616, 4,451,559, 4,427,767, 4,690,889, 4,254,212 and 4,296,199, and JP-A-61-42658.

5 Typical examples of the polymerized color-forming couplers are described in, for example, U.S.P. Nos. 3,451,820, 4,080,211, 4,367,282, 4,409,320 and 4,576,910, British Patent No. 2,102,137 and European Patent No. 341,188A.

10 The couplers capable of forming a colored dye having a suitable diffusibility are preferably those described in U.S.P. No. 4,366,237, British Patent No. 2,125,570, European Patent No. 96,570 and West German Patent (Publication) No. 3,234,533.

15 Colored couplers used for compensation for unnecessary absorption of the colored dye are preferably those described in Research Disclosure No. 17643, VII-G and No. 307105, VII-G, U.S.P. No. 4,163,670, JP-B-57-39413, U.S.P. Nos. 4,004,929 and 4,138,258 and British Patent No. 1,146,368. Other  
20 couplers preferably used herein include couplers capable of compensating for an unnecessary absorption of the colored dye with a fluorescent dye released during the coupling as described in U.S.P. No. 4,774,181 and couplers having, as a removable group,  
25 a dye precursor group capable of forming a dye by reacting with a developing agent as described in U.S.P. No. 4,777,120.

Further, compounds that release a photographically useful residue during a coupling reaction are also preferably usable in the present invention. DIR couplers which release a development inhibitor are preferably those described in the patents shown in the above described RD 17643, VII-F and No. 307105, VII-F as well as those described in JP-A's-57-151944, 57-154234, 60-184248, 63-37346 and 63-37350 and U.S.P. Nos. 4,248,962 and 4,782,012.

The couplers which release a nucleating agent or a development accelerator in the image-form in the development step are preferably those described in British Patent Nos. 2,097,140 and 2,131,188 and JP-A's-59-157638 and 59-170840. Further, compounds capable of releasing a fogging agent, development accelerator, solvent for silver halides, etc. upon the oxidation-reduction reaction with an oxidate of a developing agent as described in JP-A's-60-107029, 60-252340, 1-44940 and 1-45687 are also preferred.

Other compounds usable for the photosensitive material according to the present invention include competing couplers described in U.S.P. No. 4,130,427, polyequivalent couplers described in U.S.P. Nos. 4,283,472, 4,338,393 and 4,310,618, DIR redox compound-releasing couplers, DIR coupler-releasing couplers, DIR coupler-releasing redox compounds and DIR redox-releasing redox compounds described in



JP-A's-60-185950 and 62-24252, couplers which release a dye that restores the color after coupling-off as described in European Patent Nos. 173,302 A and 313,308 A, ligand-releasing couplers described in U.S.P. No. 4,555,477, leuco dye-releasing couplers described in JP-A-63-75747 and fluorescent dye-releasing couplers described in U.S.P. No. 4,774,181.

The couplers used in the present invention can be incorporated into the photosensitive material by various known dispersion methods.

High-boiling solvents used for an oil-in-water dispersion method are described in, for example, U.S.P. No. 2,322,027. The high-boiling organic solvents having a boiling point under atmospheric pressure of at least 175°C and usable in the oil-in-water dispersion method include, for example, phthalates (such as dibutyl phthalate, dicyclohexyl phthalate, di-2-ethylhexyl phthalate, decylphthalate, bis(2,4-di-t-amylphenyl) phthalate, bis(2,4-di-t-amylphenyl) isophthalate and bis(1,1-diethylpropyl)phthalate), phosphates and phosphonates (such as triphenyl phosphate, tricresyl phosphate, 2-ethylhexyldihenyl phosphate, tricyclohexyl phosphate, tri-2-ethylhexyl phosphate, tridodecyl phosphate, tributoxyethyl phosphate, trichloropropyl phosphate and di-2-ethylhexylphenyl phosphate), benzoates (such as 2-ethylhexyl benzoate, dodecyl benzoate and 2-ethylhexyl-p-hydroxybenzoate), amides

(such as N,N-di ethyldodecaneamide, N,N-diethyl laurylamide and N-tetradecylpyrrolidone), alcohols and phenols (such as isostearyl alcohol and 2,4-di-tert-amylphenol), aliphatic carboxylates (such as bis(2-ethylhexyl) sebacate, dioctyl azelate, glycerol tributyrates, isostearyl lactate and trioctyl citrate), aniline derivatives [such as N,N-dibutyl-2-butoxy-5-tert-octylaniline] and hydrocarbons (such as paraffin, dodecylbenzene and diisopropylnaphthalene). Co-solvents usable in the present invention include, for example, organic solvents having a boiling point of at least about 30°C, preferably 50 to about 160°C. Typical examples of them include ethyl acetate, butyl acetate, ethyl propionate, methyl ethyl ketone, cyclohexanone, 2-ethoxyethyl acetate and dimethylformamide.

The steps and effects of the latex dispersion method and examples of the latices usable for the impregnation are described in, for example, U.S.P. No. 4,199,363 and West German Patent Application (OLS) Nos. 2,541,274 and 2,541,230.

The color photosensitive material used in the present invention preferably contains phenethyl alcohol or an antiseptic or mold-proofing agent described in JP-A's-63-257747, 62-272248 and 1-80941 such as 1,2-benzisothiazolin-3-one, n-butyl p-hydroxybenzoate, phenol, 4-chloro-3,5-dimethylphenol, 2-phenoxyethanol

or 2-(4-thiazolyl) benzimidazole.

The present invention is applicable to various color photosensitive materials such as ordinary color negative films, cinema color negative films, reversal color films for slides or televisions, color papers, positive color films and reversal color papers. The present invention may be particularly preferably used as color dupe films.

Suitable supports usable in the present invention are described, for example, on page 28 of the above-described RD. No. 17643, from right column, page 647 to left column, page 648 of RD. No. 18716 and on page 879 of RD. No. 307105.

The photosensitive material of the present invention has a total thickness of the hydrophilic colloidal layers on the emulsion layer-side of 28  $\mu\text{m}$  or below, preferably 23  $\mu\text{m}$  or below, more preferably 18  $\mu\text{m}$  or below and particularly 16  $\mu\text{m}$  or below. The film-swelling rate  $T_{1/2}$  is preferably 30 sec or below, more preferably 20 sec or below. The thickness is determined at 25°C and at a relative humidity of 55% (2 days). The film-swelling rate  $T_{1/2}$  can be determined by a method known in this technical field. For example, it can be determined with a swellometer described on pages 124 to 129 of A. Green et al., "Photogr. Sci. Eng.", Vol. 19, No. 2.  $T_{1/2}$  is defined to be the time required for attaining the thickness of

a half (1/2) of the saturated film thickness (the saturated film thickness being 90% of the maximum thickness of the film swollen with the color developer at 30°C. for 3 minute 15 seconds).

5           The film-swelling rate  $T_{1/2}$  can be controlled by adding a hardener to gelatin used as the binder or by varying the time conditions after the coating.

10           The photosensitive material used in the present invention preferably has a hydrophilic colloid layer (in other words, back layer) having total thickness of 2 to 20  $\mu\text{m}$  on dry basis on the opposite side to the emulsion layer. The back layer preferably contains the above-described light absorber, filter dye, ultraviolet  
15           absorber, antistatic agent, hardener, binder, plasticizer, lubricant, coating aid, surfactant, etc. The swelling rate of the back layer is preferably 150 to 500%.

20           The color photographic light-sensitive material according to the present invention may be developed by a conventional method described in aforementioned RD. No. 17643, pages 28 to 29, ditto No. 18716, page 651, left to right columns, and ditto No. 30705, pages 880 to 881.

25           The color developer to be used in the development of the light-sensitive material of the present invention is preferably an alkaline aqueous solution containing as a main component an aromatic primary

amine color developing agent. As such a color developing agent there can be effectively used an aminophenolic compound. In particular, p-phenylenediamine compounds are preferably used.

5 Typical examples of such p-phenylenediamine compounds include 3-methyl-4-amino-N,N-diethylaniline, 3-methyl-4-amino-N-ethyl-N- $\beta$ -hydroxy-ethylaniline, 3-methyl-4-amino-N-ethyl-N- $\beta$ -methanesulfonamidoethylaniline, 3-methyl-4-amino-N-ethyl-N- $\beta$ -methoxyethylaniline, and  
10 sulfates, hydrochlorides and p-toluenesulfonates thereof. Particularly preferred among these compounds are 3-methyl-4-amino-N-ethyl-N- $\beta$ -hydroxyethylaniline sulfate. These compounds can be used in combination of two or more thereof depending on the purpose of  
15 application.

The color developer normally contains a pH buffer such as carbonate, borate and phosphate of an alkali metal or a development inhibitor or fog inhibitor such as chlorides, bromides, iodides, benzimidazoles,  
20 benzothiazoles and mercapto compounds. If desired, the color developer may further contain various preservatives such as hydroxylamine, diethylhydroxylamine, sulfites, hydrazines (e.g., N,N-biscarboxymethylhydrazine), phenylsemicarbazides, tri-  
25 ethanolamine and catecholsulfonic acids, organic solvents such as ethylene glycol and diethylene glycol, development accelerators such as benzyl alcohol,

polyethylene glycol, quaternary ammonium salts, and amines, color-forming couplers, competing couplers, auxiliary developing agents such as 1-phenyl-3-pyrazolidone, viscosity-imparting agents, various  
5 chelating agents exemplified by aminopolycarboxylic acids, aminopolyphosphonic acids, alkylphosphonic acids, and phosphonocarboxylic acids (e.g., ethylenediaminetetraacetic acid, nitrilotriacetic acid, diethylenetriaminepentaacetic acid,  
10 cyclohexanediaminetetraacetic acid, hydroxyethyliminodiacetic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, nitrilo-N,N,N-trimethylenephosphonic acid, ethylenediamine-N,N,N,N-tetramethylenephosphonic acid, and  
15 ethylenediamine-di(o-hydroxyphenylacetic acid), and salts thereof).

Further, when reversal processing is to be performed on the photographic material, color development is usually performed after black-and-white  
20 development. As the black-and-white developer, known black-and-white developers can be used singly or in combination, which include dihydroxybenzenes, such as hydroquinone, 3-pyrazolidones, such as 1-phenyl-3-pyrazolidone, or aminophenols, such as N-methyl-p-  
25 aminophenol. These black-and-white developers usually have a pH of from 9 to 12. The replenishment rate of the developer is usually 3 liter (hereinafter liter is

also referred to as "L") or less per  $m^2$  of the light-sensitive material, though depending on the type of the color photographic material to be processed. The replenishment rate may be reduced to 500 milliliter/ $m^2$  or less by decreasing the bromide ion concentration in the replenisher (hereinafter milliliter is also referred to as "mL"). If the replenishment rate is reduced, the area of the processing tank in contact with air is preferably reduced to inhibit the evaporation and air oxidation of the processing solution.

The area of the photographic processing solution in contact with air in the processing tank can be represented by an opening rate as defined by the following equation:

Opening rate = [area of processing solution in contact with air ( $cm^2$ ) / [volume of processing solution ( $cm^3$ )]

The opening rate as defined above is preferably in the range of 0.1 or less, more preferably 0.001 to 0.05. Examples of methods for reducing the opening rate include a method which comprises putting a cover such as floating lid on the surface of the processing solution in the processing tank, a method as disclosed in JP-A-1-82033 utilizing a mobile lid, and a slit development method as disclosed in JP-A-63-216050. The reduction of the opening rate is preferably effected in

both color development and black-and-white development steps as well as all the subsequent steps such as bleach, blix, fixing, washing and stabilization. The replenishment rate can also be reduced by a means for suppressing accumulation of the bromide ion in the developing solution.

The period for the color development processing usually sets between 2 to 5 min, the processing time can be shortened further by setting high pH and temperature, and using high concentration color developer.

The photographic emulsion layer that has been color-developed is normally subjected to bleach. Bleach may be effected simultaneously with fixation (i.e., blix), or these two steps may be carried out separately. For speeding up of processing, bleach may be followed by blix. Further, any of an embodiment wherein two blix baths connected in series are used, an embodiment wherein blix is preceded by fixation, and an embodiment wherein blix is followed by bleach may be selected arbitrarily according to the purpose.

Bleaching agents to be used include compounds of polyvalent metals, e.g., iron (III), peroxides, quinones, and nitro compounds. Typical examples of these bleaching agents are organic complex salts of iron (III) with, e.g., aminopolycarboxylic acids such as ethylenediaminetetraacetic acid,



diethylenetriaminepentaacetic acid,  
cyclohexanediarninetetraacetic acid, methyliminodiacetic  
acid, 1,3-diaminopropanetetraacetic acid and glycol  
ether diarninetetraacetic acid, or citric acid, tartaric  
5 acid, malic acid, etc. Of these, aminopolycarboxylic  
acid-iron (III) complex salts such as  
ethylenediaminetetraacetato iron (III) complex salts  
and 1,3-diaminopropanetetraacetato iron (III) complex  
salts are preferred in view of speeding up of  
10 processing and conservation of the environment. In  
particular, aminopolycarboxylic acid-iron (III) complex  
salts are useful in both of a bleaching solution and a  
blix solution. The pH value of a bleaching solution or  
blix solution comprising such an aminopolycarboxylic  
15 acid-iron (III) complex salts is normally in the range  
of 4.0 to 8. For speeding up of processing, the  
processing can be effected at an even lower pH value.

The bleaching bath, blix bath or a prebath thereof  
can contain, if desired, a bleaching accelerator.  
20 Examples of useful bleaching accelerators include  
compounds containing a mercapto group or a disulfide  
group as described in U.S.P. No. 3,893,858, West German  
Patents 1,290,812 and 2,059,988, JP-A's-53-32736,  
53-57831, 53-37418, 53-72623, 53-95630, 53-95631,  
25 53-104232, 53-124424, 53-141623, and 53-28426 and  
Research Disclosure No. 17129 (July 1978), thiazolidine  
derivatives as described in JP-A-51-140129, thiourea

derivatives as described in JP-B-45-8506,  
JP-A's-52-20832, and 53-32735 and U.S.P. No. 3,706,561,  
iodides as described in West German Patent 1,127,715  
and JP-A-58-16235, polyoxyethylene compounds as  
5 described in West German Patents 966,410 and 2,748,430,  
polyamine compounds as described in JP-B-45-8836,  
compounds as described in JP-A's-49-40943, 49-59644,  
53-94927, 54-35727, 55-26506 and 58-163940, and bromine  
ions. Preferred among these compounds are compounds  
10 containing a mercapto group or disulfide group because  
of their great acceleratory effects. In particular,  
the compounds disclosed in U.S.P. No. 3,893,858, West  
German Patent 1,290,812 and JP-A-53-95630 are preferred.  
The compounds disclosed in U.S.P. No. 4,552,834 are  
15 also preferred. These bleaching accelerators may be  
incorporated into the light-sensitive material. These  
bleaching accelerators are particularly effective for  
blix of color light-sensitive materials for picture  
taking.

20 The bleaching solution or blix solution preferably  
contains an organic acid besides the above mentioned  
compounds for the purpose of inhibiting bleach stain.  
A particularly preferred organic acid is a compound  
with an acid dissociation constant (pKa) of 2 to 5. In  
25 particular, acetic acid, propionic acid, hydroxyacetic  
acid, etc. are preferred.

Examples of fixing agents to be contained in the

fixing solution or blix solution include thiosulfates, thiocyanates, thioethers, thioureas, and a large amount of iodides. The thiosulfites are normally used. In particular, ammonium thiosulfate can be most widely  
5 used. Further, thiosulfates are preferably used in combination with thiocyanates, thioether compounds, thioureas, etc. As preservatives of the fixing or blix bath there can be preferably used sulfites, bisulfites, carbonyl bisulfite adducts or sulfinic acid compounds  
10 as described in European Patent 294769A. The fixing solution or blix solution preferably contains aminopolycarboxylic acids or organic phosphonic acids for the purpose of stabilizing the solution.

In the present invention, compounds having pKa of  
15 6.0 to 9.0 are preferably added to the fixing solution or a bleach-fixing solution in order to pH adjustment. Preferably, imidazoles such as imidazole, 1-methylimidazole, 1-ethylimidazole, and 2-methylimidazole are added in an amount of 0.1 to  
20 10 mol/L.

The total time required for desilvering step is preferably as short as possible so long as no maldesilvering occurs. The desilvering time is preferably in the range of 1 to 3 minutes, more  
25 preferably 1 to 2 minutes. The processing temperature is in the range of 25°C to 50°C, preferably 35°C to 45°C. In the preferred temperature range, the desilvering

rate can be improved and stain after processing can be effectively inhibited.

In the desilvering step, the agitation is preferably intensified as much as possible. Specific examples of such an agitation intensifying method include a method as described in JP-A-62-183460 which comprises jetting the processing solution to the surface of the emulsion layer in the light-sensitive material, a method as described in JP-A-62-183461 which comprises improving the agitating effect by a rotary means, a method which comprises improving the agitating effect by moving the light-sensitive material with the emulsion surface in contact with a wiper blade provided in the bath so that a turbulence occurs on the emulsion surface, and a method which comprises increasing the total circulated amount of processing solution. Such an agitation improving method can be effectively applied to the bleaching bath, blix bath or fixing bath. The improvement in agitation effect can be considered to expedite the supply of a bleaching agent, fixing agent or the like into emulsion film, resulting in an improvement in desilvering rate. The above mentioned agitation improving means can work more effectively when a bleach accelerator is used, remarkably increasing the bleach acceleration effect and eliminating the inhibition of fixing by the bleach accelerator.

The automatic developing machine to be used in the processing of the light-sensitive material of the present invention is preferably equipped with a light-sensitive material conveying means as disclosed in JP-A's-60-191257, 60-191258 and 60-191259. As described in above JP-A-60-191257, such a conveying means can remarkably reduce the amount of the processing solution carried from a bath to its subsequent bath, providing a high effect of inhibiting deterioration of the properties of the processing solution. This effect is remarkably effective for the reduction of the processing time or the amount of replenisher required at each step.

It is usual that the thus desilvered silver halide color photographic material of the present invention are subjected to washing and/or stabilization. The quantity of water to be used in the washing can be selected from a broad range depending on the characteristics of the light-sensitive material (for example, the kind of materials such as couplers, etc.), the end use of the light-sensitive material, the temperature of washing water, the number of washing tanks (number of stages), the replenishment system (e.g., counter-current system or concurrent system), and other various factors. Of these factors, the relationship between the number of washing tanks and the quantity of water in a multistage counter-current

system can be obtained according to the method described in "Journal of the Society of Motion Picture and Television Engineers", vol. 64, pp. 248-253 (May 1955).

5           According to the multi-stage counter-current system described in the above reference, although the requisite amount of water can be greatly reduced, bacteria would grow due to an increase of the retention time of water in the tank, and floating masses of  
10 bacteria stick to the light-sensitive material. In the processing for the color light-sensitive material of the present invention, in order to cope with this problem, the method of reducing calcium and magnesium ion concentrations described in JP-A-62-288838 can be  
15 used very effectively. Further, it is also effective to use isothiazolone compounds or thiabenzazoles as described in JP-A-57-8542, chlorine type bactericides, e.g., chlorinated sodium isocyanurate, benzotriazole, and bactericides described in Hiroshi Horiguchi,  
20 "Bokinbobaizai no kagaku", published by Sankyo Shuppan, (1986), Eisei Gijutsu Gakkai (ed.), "Biseibutsu no mekkin, sakkin, bobigijutsu", Kogyogijutsukai, (1982), and Nippon Bokin Bobi Gakkai (ed.), "Bokin bobizai jiten" (1986).

25           The washing water has a pH value of from 4 to 9, preferably from 5 to 8 in the processing for the light-sensitive material of the present invention. The

temperature of the water and the washing time can be selected from broad ranges depending on the characteristics and end use of the light-sensitive material, but usually ranges from 15°C to 45°C in  
5 temperature and from 20 seconds to 10 minutes in time, preferably from 25°C to 45°C in temperature and from 30 seconds to 5 minutes in time. The light-sensitive material of the present invention may be directly processed with a stabilizer in place of the washing  
10 step. For the stabilization, any of the known techniques as described in JP-A's-57-8543, 58-14834 and 60-220345 can be used.

The aforesaid washing step may be followed by stabilization in some cases. For example, a  
15 stabilizing bath containing a dye stabilizer and a surface active agent as is used as a final bath for color light-sensitive materials for picture taking can be used. Examples of such a dye stabilizer include aldehydes such as formalin and glutaraldehyde, N-  
20 methylol compounds, hexamethylenetetramine and aldehyde-bisulfite adducts. This stabilizing bath may also contain various chelating agents or antifungal agents.

The overflow accompanying replenishment of the  
25 washing bath and/or stabilizing bath can be reused in other steps such as desilvering.

In a processing using an automatic developing

machine, if the above mentioned various processing solutions are subject to concentration due to evaporation, the concentration is preferably corrected for by the addition of water.

5           The silver halide color light-sensitive material of the present invention may contain a color developing agent for the purpose of simplifying and expediting processing. Such a color developing agent is preferably used in the form of various precursors, when  
10           it is contained in the light-sensitive material. Examples of such precursors include indoaniline compounds as described in U.S.P. No. 3,342,597, Schiff's base type compounds as described in U.S.P. No. 3,342,599, and Research Disclosure Nos. 14,850 and  
15           15,159, and aldol compounds as described in Research Disclosure No. 13,924, metal complexes as described in U.S.P. No. 3,719,492, and urethane compounds as described in JP-A-53-135628.

          The silver halide color light-sensitive material  
20           of the present invention may optionally comprise various 1-phenyl-3-pyrazolidones for the purpose of accelerating color development. Typical examples of such compounds are described in JP-A's-56-64339, 57-144547 and 58-115438.

25           In the present invention, the various processing solutions are used at a temperature of 10°C to 50°C. The standard temperature range is normally from 33°C to



38°C. However, a higher temperature range can be used to accelerate processing, reducing the processing time. On the contrary, a lower temperature range can be used to improve the picture quality or the stability of the processing solutions.

Further, the silver halide lightsensitive material of the invention may be applied to heat-development lightsensitive material as described, for example, in U.S.P. No. 4,500,626, and JP-A's-60-133449, 59-218443 and 61-238056, and European Patent 210 660A2.

Further, the silver halide color photographic lightsensitive material of the invention can exhibit advantages easily when it is applied to lens-fitted film unit described, for example, in Jap. Utility Model KOKOKU Publication Nos. 2-32615 and 3-39784, which is effective.

#### Example

The present invention will be specifically described by examples below. However, the present invention is not limited to there examples.

#### (Example 1)

Silver halide emulsions Em-A1 to -A11 were prepared by the following preparation methods.

#### (Em-A1)

42.2L of an aqueous solution containing 31.7g of low-molecular-weight gelatin phthalated at a phthalation ratio of 97% and 31.7g of KBr were vigorously

stirred at 35°C. 1,583 mL of an aqueous solution containing 316.7g of AgNO<sub>3</sub> and 1,583 mL of an aqueous solution containing 221.5g of KBr and 52.7g of low-molecular weight gelatin having a molecular weight of 15,000 were added over 1 min by the double jet method. Immediately after the addition, 52.8g of KBr were added, and 2,485 mL of an aqueous solution containing 398.2g of AgNO<sub>3</sub> and 2,581 mL of an aqueous solution containing 291.1g of KBr were added over 2 min by the double jet method. Immediately after the addition, 47.8g of KBr were added. After that, the temperature was raised to 40°C to ripen the material. After the ripening, 923g of phthalated gelatin whose phthalation ratio is 97% and molecular weight is 100,000 and 79.2g of KBr were added, and 15,947 mL of an aqueous solution containing 5,103g of AgNO<sub>3</sub> and an aqueous KBr solution were added over 12 min by the double jet method while the flow rate was accelerated such that the final flow rate was 1.4 times the initial flow rate. During the addition, silver potential was maintained at -60mV against a saturated calomel electrode. After washing with water, gelatin was added, the pH and the pAg were adjusted to 5.7 and 8.8, respectively, and the weight in terms of silver of the emulsion and the gelatin amount were adjusted to 131.8g and 64.1g, respectively, per kg of the emulsion, thereby preparing a seed emulsion.

1,211 mL of an aqueous solution containing 46g of

phthalated gelatin whose phthalation ratio is 97% and 1.7g of KBr was vigorously stirred at 75°C. After 9.9g of the above-mentioned seed emulsion were added, 0.3g of modified silicone oil (L7602 manufactured by Nippon Uniker K.K.) was added. H<sub>2</sub>SO<sub>4</sub> was added to adjust the pH to 5.5, and 67.6 mL of an aqueous solution containing 7.0g of AgNO<sub>3</sub> and an aqueous KBr solution were added over 6 min by the double jet method while the flow rate was accelerated such that the final flow rate was 5.1 times the initial flow rate. During the addition, the silver potential was maintained at -20mV against a saturated calomel electrode. After 2 mg of sodium benzenethiosulfonate and 2 mg of thiourea dioxide were added, 410 mL of an aqueous solution containing 144.5g of AgNO<sub>3</sub> and a mixed aqueous KBr and KI solution containing 7 mol% of KI were added over 56 min by the double jet method while the flow rate was accelerated such that the final flow rate was 3.7 times the initial flow rate. During the addition, the silver potential was maintained at -30mV against a calomel electrode. 121.3mL of an aqueous solution containing 45.6g of AgNO<sub>3</sub> and a KBr solution were added by the double jet method over 22 min. During the addition, the silver potential was maintained at +20mV against a saturated calomel electrode. The temperature was raised to 82°C, followed by adjustment of the silver potential at -80mV by an addition of KBr, an AgI fine

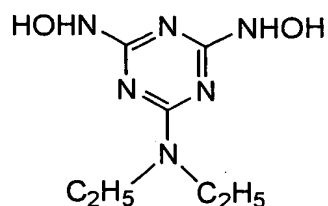
grain emulsion having a grain size of  $0.037 \mu\text{m}$  was added in an amount of 6.33g in terms of silver.

Immediately after the addition, 206.2mL of an aqueous solution containing 66.4g of  $\text{AgNO}_3$  was added over 16

5 min. The silver potential was maintained at -80mV with a KBr solution for the initial period of the addition of 5 min. After washing with water, gelatin comprising, in an amount of 30%, components each having a molecular weight measured according to the PAGI method of 280,000 or more was added, and the pH and the pAg were adjusted to 5.8 and 8.7, respectively, at  $40^\circ\text{C}$ .

After compounds 11 and 12 were added, temperature was raised to  $60^\circ\text{C}$ . After sensitizing dyes 11 and 12 were added, potassium thiocyanate, chloroauric acid, sodium thiosulfate, and N,N-dimethylselenourea were added to optimally perform chemical sensitization. At the end of this chemical sensitization, compounds 13 and 14 were added. "Optimal chemical sensitization" herein means that the addition amount of each of the sensitizing dyes and the compounds was  $10^{-1}$  to  $10^{-8}$  mol per mol of a silver halide.

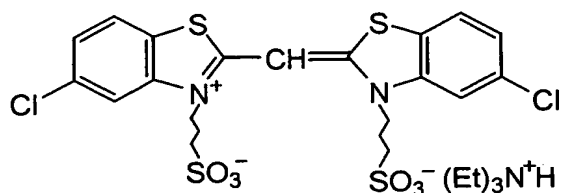
Compound 11



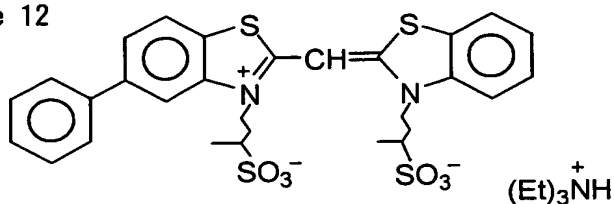
Compound 12



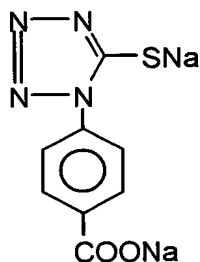
Sensitizing dye 11



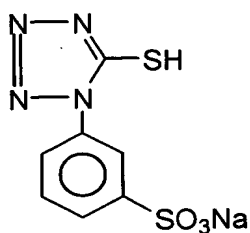
Sensitizing dye 12



Compound 13



Compound 14



The thus obtained grains were observed with a transmission electron microscope while cooling them with liquid nitrogen to find that 10 or more dislocation lines per grain were observed near side faces thereof.

(Em-A2)

Emulsion Em-A2 was prepared in the same manner as (Em-A1), except that compound (I-13) of the invention was added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time of chemical sensitization.

5 (Em-A3)

Emulsion Em-A3 was prepared in the same manner as (Em-A2), except that compound (IX-2-3) of the invention was added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time of chemical sensitization.

10 (Em-A4)

After 9.9g of the above-mentioned seed emulsion were added, 0.3g of modified silicone oil (L7602 manufactured by Nippon Uniker K.K.) was added.  $H_2SO_4$  was added to adjust the pH to 5.5, and 67.6 mL of an aqueous solution containing 7.0g of  $AgNO_3$  and an aqueous KBr solution were added over 6 min by the double jet method while the flow rate was accelerated such that the final flow rate was 5.1 times the initial flow rate. During the addition, the silver potential was maintained at -20mV against a saturated calomel electrode. After 2 mg of sodium benzenethiosulfonate and 2 mg of thiourea dioxide were added, 381 mL of an aqueous solution containing 134.4g of  $AgNO_3$  and an aqueous KBr solution were added over 56 min by the double jet method while the flow rate was accelerated such that the final flow rate was 3.7 times the initial flow rate. At this time, an AgI fine grain emulsion

having a grain size of  $0.037\ \mu\text{m}$  was simultaneously added so that the silver iodide content became 7 mol% while accelerating the flow rate, and the silver potential was maintained at  $-30\text{mV}$  against a saturated calomel electrode. 121.3mL of an aqueous solution containing 45.6g of  $\text{AgNO}_3$  and a KBr solution were added by the double jet method over 22 min. During the addition, the silver potential was maintained at  $+20\text{mV}$  against a saturated calomel electrode. The temperature was raised to  $82^\circ\text{C}$ , followed by adjustment of the silver potential at  $-80\text{mV}$  by an addition of KBr, an AgI fine grain emulsion having a grain size of  $0.037\ \mu\text{m}$  was added in an amount of 6.33g in terms of silver. Immediately after the addition, 206.2mL of an aqueous solution containing 66.4g of  $\text{AgNO}_3$  was added over 16 min. The silver potential was maintained at  $-80\text{mV}$  with a KBr solution for the initial period of the addition of 5 min. After washing with water, gelatin comprising, in an amount of 30%, components each having a molecular weight measured according to the PAGI method of 280,000 or more was added, and the pH and the pAg were adjusted to 5.8 and 8.7, respectively, at  $40^\circ\text{C}$ . The same procedure as in Em-A1 was conducted after this.

The thus obtained grains were observed with a transmission electron microscope while cooling them with liquid nitrogen to find that 10 or more dislocation lines per grain were observed near side

faces thereof.

(Em-5)

Emulsion Em-A5 was prepared in the same manner as (Em-A4), except that compound (I-13) of the invention  
5 was added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time of chemical sensitization.

(Em-6)

Emulsion Em-A6 was prepared in the same manner as (Em-A4), except that compound (IX-2-3) of the invention  
10 was added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time of chemical sensitization.

(Em-7)

After 9.9g of the above-mentioned seed emulsion were added, 0.3g of modified silicone oil (L7602  
15 manufactured by Nippon Uniker K.K.) was added.  $H_2SO_4$  was added to adjust the pH to 5.5, and 67.6 mL of an aqueous solution containing 7.0g of  $AgNO_3$  and an aqueous KBr solution were added over 6 min by the double jet method while the flow rate was accelerated  
20 such that the final flow rate was 5.1 times the initial flow rate. During the addition, the silver potential was maintained at -20mV against a saturated calomel electrode. After 2 mg of sodium benzenethiosulfonate and 2 mg of thiourea dioxide were added, 381 mL of  
25 an aqueous solution containing 134.4g of  $AgNO_3$  and an aqueous KBr solution were added over 56 min by the double jet method while the flow rate was accelerated



such that the final flow rate was 3.7 times the initial flow rate. At this time, an AgI fine grain emulsion having a grain size of  $0.037\ \mu\text{m}$  was simultaneously added so that the silver iodide content became 7 mol% while accelerating the flow rate, and the silver potential was maintained at -30mV against a saturated calomel electrode. 121.3mL of an aqueous solution containing 45.6g of  $\text{AgNO}_3$  and a KBr solution were added by the double jet method over 22 min. During the addition, the silver potential was maintained at +20mV against a saturated calomel electrode. The temperature was decreased to  $40^\circ\text{C}$ , followed by adjustment of the silver potential at -40mV by an addition of KBr, then, an aqueous solution containing 14.5g of sodium p-iodoacetamidobenzenesulfonate mono-hydrate was added, followed by adding 57mL of 0.8M aqueous sodium sulfite solution with a constant flow rate for 1 min, while maintaining the pH at 9.0, thereby iodide ions were made to generate. After 2 min, the temperature was raised to  $55^\circ\text{C}$  over 15 min and the pH was returned to 5.5. After that, 206.2mL of an aqueous solution containing 66.4g of  $\text{AgNO}_3$  was added over 16 min. During the addition, the silver potential was maintained at -50mV with a KBr solution. After washing with water, gelatin comprising, in an amount of 30%, components each having a molecular weight measured according to the PAGI method of 280,000 or more was

added, and the pH and the pAg were adjusted to 5.8 and 8.7, respectively, at 40°C. The same procedure as in Em-A1 was conducted after this.

5 The thus obtained grains were observed with a transmission electron microscope while cooling them with liquid nitrogen to find that 10 or more dislocation lines per grain were observed near side faces thereof. The dislocation lines positioned at the periphery portion were localized near corner portions  
10 of the tabular grains.

(Em-A8)

Emulsion Em-A8 was prepared in the same manner as (Em-A7), except that each of compounds (I-13) and (IX-2-3) of the invention were added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time of chemical sensitization.  
15

(Em-A9)

Emulsion Em-A9 was prepared in the same manner as (Em-A7), except that compound (IX-2-3) of the invention was added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the  
20 time of chemical sensitization.

(Em-A10)

After 9.9g of the above-mentioned seed emulsion were added, 0.3g of modified silicone oil (L7602 manufactured by Nippon Uniker K.K.) was added.  $H_2SO_4$   
25 was added to adjust the pH to 5.5, and 67.6 mL of an aqueous solution containing 7.0g of  $AgNO_3$  and an aqueous KBr solution were added over 6 min by the

double jet method while the flow rate was accelerated such that the final flow rate was 5.1 times the initial flow rate. During the addition, the silver potential was maintained at -20mV against a saturated calomel electrode. After 2 mg of sodium benzenethiosulfonate and 2 mg of thiourea dioxide were added, 381 mL of an aqueous solution containing 134.4g of  $\text{AgNO}_3$  and an aqueous KBr solution were added over 56 min by the double jet method while the flow rate was accelerated such that the final flow rate was 3.7 times the initial flow rate. At this time, an AgI fine grain emulsion having a grain size of  $0.037 \mu\text{m}$  was simultaneously added so that the silver iodide content became 7 mol% while accelerating the flow rate, and the silver potential was maintained at -30mV against a saturated calomel electrode. 330.8mL of an aqueous solution containing 102.4g of  $\text{AgNO}_3$  and a KBr solution were added by the double jet method over 60 min. During the addition, the silver potential for the initial 50 min was maintained at +20mV, and the remaining 10 min was maintained at 120mV against a saturated calomel electrode. The temperature was raised to  $50^\circ\text{C}$ , 55mL of 0.3% aqueous KI solution was added over 10 min. Immediately after this, 100mL of an aqueous solution containing 14.2g of  $\text{AgNO}_3$ , 120mL of an aqueous solution containing 2.1g of NaCl and 4.17g of KBr, and a solution containing 0.0133mol of AgI fine grains were

added simultaneously. At this time,  $9.4 \times 10^{-4}$  mol of  $K_4[RuCN]_6$  per mol of  $AgNO_3$  being added were made to present. After that, a sensitizing dye was added, in order to stabilization of epitaxial. After washing  
5 with water, gelatin comprising, in an amount of 30%, components each having a molecular weight measured according to the PAGI method of 280,000 or more was added, and the pH and the pAg were adjusted to 5.8 and 8.7, respectively, at 40°C. The same procedure as in  
10 Em-A1 was conducted after this.

The thus obtained grains were observed with a transmission electron microscope while cooling them with liquid nitrogen to find that epitaxial phase was joined at corner portion of the tabular grains.

15 (Em-A11)

Emulsion Em-A11 was prepared in the same manner as (Em-A10), except that each of compounds (I-13) and (IX-2-3) of the invention was added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time of chemical sensitization.

20 (Em-A12)

Emulsion Em-A12 was prepared in the same manner as (Em-A10), except that compound (IX-2-3) of the invention was added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time of chemical sensitization.

25 (Em-A13)

After 9.9g of the above-mentioned seed emulsion were added, 0.3g of modified silicone oil (L7602

manufactured by Nippon Uniker K.K.) was added.  $\text{H}_2\text{SO}_4$  was added to adjust the pH to 5.5, and 67.6 mL of an aqueous solution containing 7.0g of  $\text{AgNO}_3$  and an aqueous KBr solution were added over 6 min by the

5 double jet method while the flow rate was accelerated such that the final flow rate was 5.1 times the initial flow rate. During the addition, the silver potential was maintained at -20mV against a saturated calomel electrode. After 2 mg of sodium benzenethiosulfonate

10 and 2 mg of thiourea dioxide were added, an AgBrI fine grain emulsion (average grain size:  $0.015 \mu\text{m}$ ) having a silver iodide content of 7 mol% was added over 90 min to the reaction vessel while preparing the fine grain emulsion in a mixing apparatus provide outside the

15 reaction vessel. In the mixing apparatus, 762mL of an aqueous solution containing 134.4g of  $\text{AgNO}_3$  and 762mL of aqueous solution containing 90.1g of KBr, 9.46g of KI and 38.1g of gelatin having a molecular weight of 20,000 were added simultaneously to prepare the

20 emulsion. During the addition, the silver potential was maintained at -30mV against a saturated calomel electrode. 121.3mL of an aqueous solution containing 45.6g of  $\text{AgNO}_3$  and a KBr aqueous solution were added by the double jet method over 22 min. During the addition,

25 the silver potential was maintained at +20mV against a saturated calomel electrode. The temperature was raised to  $82^\circ\text{C}$ , and the silver potential was adjusted

to -80mV by the addition of KBr, then an AgI fine grain emulsion having a grain size of  $0.037 \mu\text{m}$  was added in an amount of 6.33 g in terms of KI weight. Immediately after the addition, 206.2mL of an aqueous solution  
5 containing 66.4g of  $\text{AgNO}_3$  was added over 16 min. The silver potential was maintained at -80mV with a KBr solution for the initial period of the addition of 5 min. After washing with water, gelatin comprising, in an amount of 30%, components each having a molecular  
10 weight measured according to the PAGI method of 280,000 or more was added, and the pH and the pAg were adjusted to 5.8 and 8.7, respectively, at  $40^\circ\text{C}$ . The same procedure as in Em-A1 was conducted after this.

The thus obtained grains were observed with a  
15 transmission electron microscope while cooling them with liquid nitrogen to find that 10 or more dislocation lines were observed near side faces thereof.

(Em-A14)

Emulsion Em-A14 was prepared in the same manner as  
20 (Em-A13), except that each of compounds (I-13) and (IX-2-3) of the invention was added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time of chemical sensitization.

(Em-A15)

Emulsion Em-A15 was prepared in the same manner as  
25 (Em-A13), except that compound (IX-2-3) of the invention was added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time of chemical sensitization.

(Em-B: Emulsion for a low-speed blue sensitive layer)

1192 mL of an aqueous solution containing 0.96g of a low-molecular-weight gelatin and 0.9g of KBr was  
5 vigorously agitated while maintaining the temperature at 40°C. 37.5 mL of an aqueous solution containing 1.49g of AgNO<sub>3</sub> and 37.5 mL of an aqueous solution containing 1.5g of KBr were added by the double jet method over a period of 30 sec. After 1.2g of KBr was  
10 added, the temperature was raised to 75°C, and the mixture was ripened. After full ripening, 30g of trimellitated gelatin whose amino groups are chemically modified with trimellitic acid and having a molecular weight of 100,000 was added, and the pH was adjusted to  
15 7. 6mg of thiourea dioxide was added. An aqueous solution of KBr and 116 mL of an aqueous solution containing 29g of AgNO<sub>3</sub> were added by the double jet method while increasing the flow rate so that the final flow rate became 3 times the initial flow rate. During  
20 this period, the silver potential was maintained at -20 mV against saturated calomel electrode. Further, 440.6mL of an aqueous solution containing 110.2g of AgNO<sub>3</sub> and an aqueous solution of KBr were added by the double jet method over a period of 30 min while  
25 increasing the flow rate so that the final flow rate was 5.1 times the initial flow rate. During this period, the AgI fine grain emulsion used in the

preparation of Em-A1 was simultaneously added while  
conducting a flow rate increase so that the silver  
iodide content was 15.8 mol%, and the silver potential  
was maintained at 0 mV against saturated calomel  
5 electrode. An aqueous solution of KBr and 96.5 mL  
of an aqueous solution containing 24.1g of  $\text{AgNO}_3$  were  
added by the double jet method over a period of 3 min.  
During the addition the silver potential was maintained  
at 0mV. After 26mg of sodium ethythiosulfonate was  
10 added, the temperature was raised to  $55^\circ\text{C}$ , and the  
silver potential was adjusted to -90mV by adding a KBr  
solution. 8.5g in terms of KI weight of the  
aforementioned AgI fine grain emulsion was added.  
Immediately after the addition, 228mL of an aqueous  
15 solution containing 57g of  $\text{AgNO}_3$  was added over 5 min.  
At this time the silver potential at the completion of  
the addition was adjusted to +20mV by a KBr aqueous  
solution. The emulsion was washed with water and  
chemically sensitized in almost the same manner as in  
20 Em-A1.

(Em-C: Emulsion for a low-speed blue sensitive  
layer)

1192 mL of an aqueous solution containing 1.02g of  
phthalated gelatin whose phthalation ratio is 97%,  
25 molecular weight is 100,000 and containing  $35\mu\text{mol}$  of  
methionine per g and 0.97g of KBr, was vigorously  
agitated while maintaining the temperature at  $35^\circ\text{C}$ . 42



mL of an aqueous solution containing 4.47g of  $\text{AgNO}_3$  and 42 mL of an aqueous solution containing 3.16g of KBr were added by the double jet method over a period of 9 sec. After 2.6g of KBr was added, the temperature was raised to  $66^\circ\text{C}$ , and the mixture was thoroughly ripened. After full ripening, 41.2g of trimellitated gelatin used in the preparation of Em-B and having a molecular weight of 100,000, and 18.5g of NaCl were added. After the pH was adjusted to 7.2, 8mg of dimethylaminborane was added. An aqueous solution of KBr and 203 mL of an aqueous solution containing 26g of  $\text{AgNO}_3$  were added by the double jet method while increasing the flow rate so that the final flow rate became 3.8 times the initial flow rate. During this period, the silver potential was maintained at -30 mV against saturated calomel electrode. Further, 440.6mL of an aqueous solution containing 110.2g of  $\text{AgNO}_3$  and an aqueous solution of KBr were added by the double jet method over a period of 24 min while increasing the flow rate so that the final flow rate was 5.1 times the initial flow rate. During this period, the AgI fine grain emulsion used in the preparation of Em-A1 was simultaneously added while conducting a flow rate increase so that the silver iodide content was 2.3 mol%, and the silver potential was maintained at -20 mV against saturated calomel electrode. After 10.7mL of 1N aqueous solution of potassium thiocyanate was added, an aqueous solution of

KBr and 153.5 mL of an aqueous solution containing 24.1g of  $\text{AgNO}_3$  were added by the double jet method over a period of 2 min 30 sec. During the addition the silver potential was maintained at 10mV. The silver potential was maintained at 10mV. The silver potential was adjusted to -70 mV by adding a KBr solution. 6.4g in terms of KI weight of the aforementioned AgI fine grain emulsion was added. Immediately after the addition, 404mL of an aqueous solution containing 57g of  $\text{AgNO}_3$  was added over 45 min. At this time the silver potential at the completion of the addition was adjusted to -20mV by a KBr aqueous solution. The emulsion was washed with water and chemically sensitized in almost the same manner as in Em-A1.

(Em-D: Emulsion for a low-speed blue sensitive layer)

Em-D was prepared by changing the addition amount of  $\text{AgNO}_3$  at nucleation to twice. Further, the potential at the completion of the addition of the 404 mL final solution containing 57g of  $\text{AgNO}_3$ , was changed to +90mV, by adjusting the KBr solution. Other conditions were almost the same as for Em-C.

(Em-E: Magenta color layer having a spectral sensitivity peak in a region of 480 to 550 nm. A layer imparting inter-layer effect on red-sensitive layer)

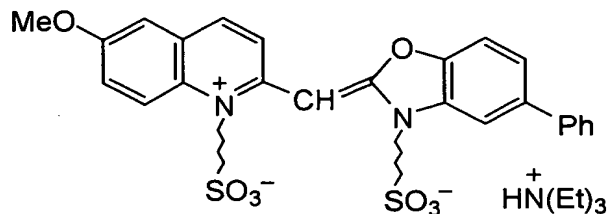
1,200 mL of an aqueous solution containing 0.71g of low molecular weight gelatin having molecular weight

of 15,000, 0.92g of KBr and 0.2g of the modified  
silicone oil used in the preparation of the Em-A1 were  
held at 39°C and stirred with violence at pH 1.8. An  
aqueous solution containing 0.45g of AgNO<sub>3</sub> and an  
5 aqueous KBr solution containing 1.5 mol% of KI were  
added over 17 sec by the double jet method. During the  
addition, the excess KBr concentration was held  
constant. The temperature was raised to 56°C to ripen  
the material. After through ripening, 20g of  
10 phthalated gelatin having a phthalation ratio of 97%,  
molecular weight of 100,000, and containing 35μm of  
methionine per gram, was added. After the pH was  
adjusted to 5.9, 2.9g of KBr were added. 288 mL of an  
aqueous solution containing 28.8g of AgNO<sub>3</sub> and an  
15 aqueous KBr solution were added over 53 min by the  
double jet method. During the addition, the AgI fine  
grain emulsion used in the preparation of Em-A1 was  
simultaneously added such that the silver iodide  
content was 4.1 mol% and the silver potential was  
20 maintained at -60mV against calomel electrode. After  
2.5g of KBr were added, an aqueous solution containing  
87.7g of AgNO<sub>3</sub> and an aqueous KBr solution were added  
over 63 min by the double jet method while the flow  
rate was accelerated so that the final flow rate was  
25 1.2 times the initial flow rate. During the addition,  
the aforementioned AgI fine grain emulsion was  
simultaneously added at an accelerated flow rate such

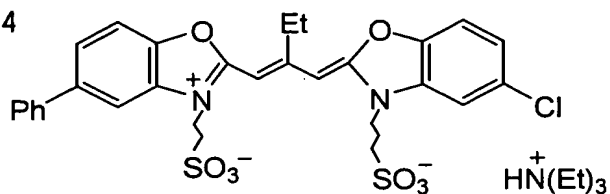
that the silver iodide content was 10.5 mol%, and the silver potential was maintained at -70mV. After 1 mg of thiourea dioxide was added, 132 mL of an aqueous solution containing 41.8g of AgNO<sub>3</sub> and an aqueous KBr solution were added over 25 min by the double jet method. The addition of the aqueous KBr solution was so adjusted that the silver potential at the completion of the addition was +20mV. After 2mg of sodium benzenethiosulfonate was added, pH was adjusted to 7.3. After KBr was added to adjust the silver potential at -70mV, the above-mentioned AgI fine grain emulsion was added in an amount of 5.73g in terms of a KI weight. Immediately after the addition, 609 mL of an aqueous solution containing 66.4g of AgNO<sub>3</sub> were added over 10 min. For the first 6 min of the addition, the silver potential was held at -70mV by a KBr solution. The resultant emulsion was washed with water, then gelatin was added. The pH and pAg of the mixture was adjusted to 6.5 and 8.2, respectively, at 40°C. After compounds 11 and 12 were added, the temperature was raised to 56°C. After 0.0004 mol of the above-mentioned AgI fine grains, per mol of silver, were added sensitizing dyes 13 and 14 were added. Chemical sensitization was optimally performed by addition of potassium thiocyanate, chloroauric acid, sodium thiosulfonate and N,N-dimethylselenourea. At the completion of the chemical sensitization, compounds 13

and 14 were added.

Sensitizing dye 13



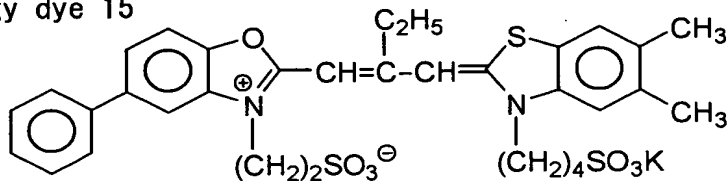
Sensitizing dye 14



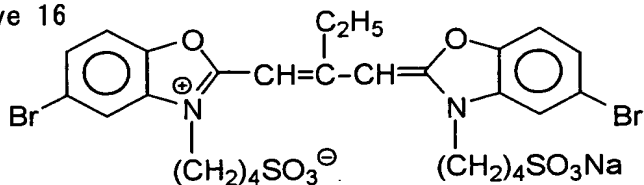
(Em-F: Emulsion for a medium-speed green sensitive layer)

5 Em-F was prepared in almost the same manner as Em-E, except that the addition amount of  $\text{AgNO}_3$  during nucleation was changed to 3.1 times. Also, the sensitizing dyes used for Em-E were changed to sensitizing dyes 15, 16 and 17.

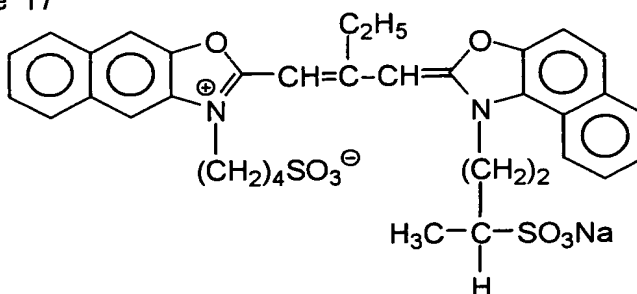
Sensitizing dye 15



Sensitizing dye 16



Sensitizing dye 17



(Em-G: Emulsion for a low-speed green sensitive layer)

1,200 mL of an aqueous solution containing 0.70g of low molecular weight gelatin having molecular weight of 15,000, 0.9g of KBr, 0.175g of KI and 0.2g of the modified silicone oil used in the preparation of the Em-A1 were held at 33°C and stirred with violence at pH 1.8. An aqueous solution containing 1.8g of AgNO<sub>3</sub> and an aqueous KBr solution containing 3.2 mol% of KI were added over 9 sec by the double jet method. During the addition, the excess KBr concentration was held constant. The temperature was raised to 69°C to ripen the material. After completion of ripening, 27.8g of trimellitated gelatin whose amino groups were modified with trimellitic acid, having molecular weight of 100,000 and containing 35  $\mu$ m, per gram, of methionine was added. After the pH was adjusted to 6.3, 2.9g of

KBr were added. 270 mL of an aqueous solution containing 27.58g of  $\text{AgNO}_3$  and an aqueous KBr solution were added over 37 min by the double jet method. At this time, an AgI fine grain emulsion having a grains  
5 size of  $0.008 \mu\text{m}$ , which was prepared immediately before the addition thereof in a separate chamber furnished with a magnetic coupling induction type agitator as described in JP-A-10-43570, by mixing a low-molecular-weight gelatin whose molecular weight  
10 was 15,000, an aqueous solution of  $\text{AgNO}_3$  and an aqueous solution of KI, was simultaneously added, so that the silver iodide content was 4.1 mol%. Further, the silver potential was maintained at -60mV against calomel electrode. After 2.6g of KBr were added, an  
15 aqueous solution containing 87.7g of  $\text{AgNO}_3$  and an aqueous KBr solution were added over 49 min by the double jet method while the flow rate was accelerated so that the final flow rate was 3.1 times the initial flow rate. During the addition, the aforementioned AgI  
20 fine grain emulsion was simultaneously added at an accelerated flow rate such that the silver iodide content was 7.9 mol%, and the silver potential was maintained at -70mV. After 1 mg of thiourea dioxide was added, 132 mL of an aqueous solution containing  
25 41.8g of  $\text{AgNO}_3$  and an aqueous KBr solution were added over 20 min by the double jet method. The addition of the aqueous KBr solution was so adjusted that the

silver potential at the completion of the addition was +20mV. The temperature was raised to 78°C, and the pH was adjusted to 9.1, then, the potential was set to -60 mV by the addition of KBr. The AgI fine grain emulsion  
5 used in the preparation of Em-A1 was added in an amount of 5.73g in terms of a KI weight. Immediately after the addition, 321 mL of an aqueous solution containing 66.4g of AgNO<sub>3</sub> were added over 4 min. For the first 2 min of the addition, the silver potential was held at  
10 -60mV by a KBr solution. The resultant emulsion was washed with water and chemically sensitized almost the same manner as in Em-F.

(Em-H: Emulsion for a low-speed green sensitive layer)

15 An aqueous solution containing 17.8g of ion-exchanged gelatin having a molecular weight of 100,000, 6.2g of KBr, and 0.46g of KI was vigorously agitated while maintaining the temperature at 45°C. An aqueous solution containing 1.85g of AgNO<sub>3</sub> and an aqueous  
20 solution containing 3.8g of KBr were added by the double jet method over a period of 47 sec. After the temperature was raised to 63°C, 24.1g of ion-exchanged gelatin having a molecular weight of 100,000 was added to ripen. After through ripening, an aqueous solution  
25 of KBr and an aqueous solution containing 133.4g of AgNO<sub>3</sub> were added by the double jet method over a period of 20 min while increasing the flow rate so that the



final flow rate was 2.6 times the initial flow rate. During this period, the silver potential was maintained at +40mV against calomel electrode. Further, 0.1mg of  $K_2IrCl_6$  was added 10 min after the initiation of the addition. After 7g of NaCl was added, an aqueous solution containing 45.6g of  $AgNO_3$  and a KBr solution were added by the double jet method over 12 min. During this period, the silver potential was maintained at +90mV. Further, 100 mL of an aqueous solution containing 29mg of yellow prussiate of potash was added over 6 min from the initiation of the addition. After 14.4g of KBr was added, the AgI fine grain emulsion used for the preparation of Em-A1 was added in an amount of 6.3g in terms of KI amount. Immediately after the addition, an aqueous solution containing 42.7g of  $AgNO_3$  and a KBr solution were added by the double jet method over 11 min. During this period, the silver potential was held at +90mV. The resultant emulsion was washed with water and chemically sensitized almost the same manner as in Em-F.

(Em-I: Emulsion for a high-speed red sensitive layer)

Em-I was prepared by almost the same manner as Em-H, except that the temperature at nucleation was changed to 38°C.

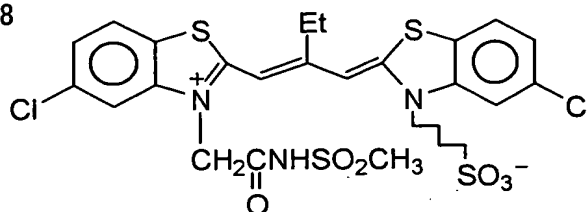
(Em-J1: Emulsion for a high-speed red sensitive layer)

1200 mL of an aqueous solution containing 0.38g of phthalated gelatin having a molecular weight of 100,000 and a phthalation rate of 97%, and 0.99g of KBr was vigorously agitated while maintaining the temperature at 60°C and the pH at 2. An aqueous solution containing 1.96g of AgNO<sub>3</sub> and an aqueous solution containing 1.97g of KBr and 0.172g of KI were added by the double jet method over a period of 30 sec. After the completion of ripening, 12.8g of trimellitated gelatin whose amino groups were modified with trimellitic acid, having molecular weight of 100,000 and containing 35  $\mu$ mol, per gram, of methionine was added. After the pH was adjusted to 5.9, 2.99g of KBr and 6.2g of NaCl were added. 60.7mL of an aqueous solution containing 27.3g of AgNO<sub>3</sub> and a KBr solution were added by the double jet method over 35 min. During this period, the silver potential was maintained at -50mV against saturated calomel electrode. An aqueous solution of KBr and an aqueous solution containing 65.6g of AgNO<sub>3</sub> were added by the double jet method over a period of 37 min while increasing the flow rate so that the final flow rate was 2.1 times the initial flow rate. During this period, the AgI fine grain emulsion used for the preparation of Em-A1 was simultaneously added with an accelerated flow rate so that the silver iodide content was 6.5 mol%, and the silver potential was maintained at -50mV. After 1.5g

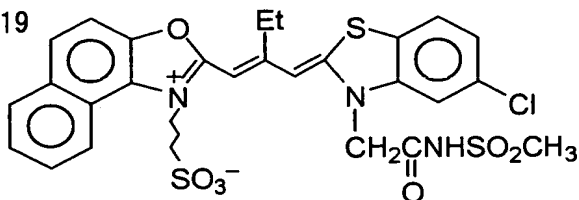
of thiourea dioxide was added, 132mL of an aqueous solution containing 41.8g of  $\text{AgNO}_3$  and an KBr solution were added by the double jet method over 13 min. The addition of KBr solution was so adjusted that silver potential at the completion of the addition was +40mV. After 2mg of sodium benzenethiosulfonate was added, KBr was added to adjust the silver potential to -100mV. The above-mentioned AgI fine grain emulsion was added in an amount of 6.2g in terms of KI weight.

Immediately after the addition, 300mL of an aqueous solution containing 88.5g of  $\text{AgNO}_3$  was added over 8 min. The addition of a KBr solution was so adjusted that the potential at the completion of the addition was +60mV. After washing the mixture with water, gelatin was added, and pH and pAg were adjusted to 6.5 and 8.2, respectively at 40°C. After addition of compounds 11 and 12, the temperature was raised to 61°C. After sensitizing dyes 18, 19, 20 and 21 were added,  $\text{K}_2\text{IrCl}_6$ , potassium thiocyanate, chlorauric acid, sodium thiosulfonate and N,N-dimethylselenourea were added to perform optimal chemical sensitization. At the completion of the chemical sensitization, compounds 13 and 14 were added.

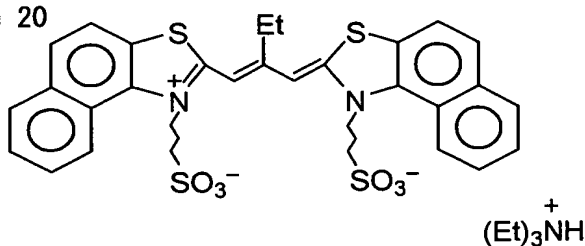
Sensitizing dye 18



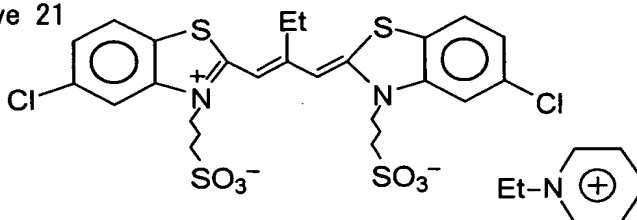
Sensitizing dye 19



Sensitizing dye 20



Sensitizing dye 21



(Em-J2)

Em-J2 was prepared in the same manner as Em-J1,  
5 except that compound (I-13) of the invention was added  
in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time of  
chemical sensitization.

(Em-J3)

Em-J3 was prepared in the same manner as Em-J1,  
10 except that compound (IX-2-50) of the invention was  
added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time  
of chemical sensitization.

(Em-J4 to Em-J8)

Em-J4 to Em-J8 were prepared in the same manner as Em-J1, except that compound (IV-2) of the invention was added at the time of chemical sensitization so that the contents thereof with respect to the sensitizing dyes were those as set forth in Table 1, respectively.

(Em-J9 to Em-J13)

Em-J9 to Em-J13 were prepared in the same manner as Em-J2, except that compound (IV-2) of the invention was added at the time of chemical sensitization so that the contents thereof with respect to the sensitizing dyes were those as set forth in Table 1, respectively.

(Em-J14)

1200 mL of an aqueous solution containing 0.38g of phthalated gelatin having a molecular weight of 100,000 and a phthalation rate of 97%, and 0.99g of KBr was vigorously agitated while maintaining the temperature at 60°C and the pH at 2. An aqueous solution containing 1.96g of AgNO<sub>3</sub> and an aqueous solution containing 1.97g of KBr and 0.172g of KI were added by the double jet method over a period of 30 sec. After the completion of ripening, 12.8g of trimellitated gelatin whose amino groups were modified with trimellitic acid, having molecular weight of 100,000 and containing 35  $\mu$ mol, per gram, of methionine was added. After the pH was adjusted to 5.9, 2.99g of KBr and 6.2g of NaCl were added. 60.7mL of an aqueous

solution containing 27.3g of  $\text{AgNO}_3$  and a KBr solution were added by the double jet method over 35 min. During this period, the silver potential was maintained at -50mV against saturated calomel electrode.

- 5 An aqueous solution of KBr and an aqueous solution containing 65.6g of  $\text{AgNO}_3$  were added by the double jet method over a period of 37 min while increasing the flow rate so that the final flow rate was 2.1 times the initial flow rate. During this period, the AgI fine grain emulsion used for the preparation of Em-A1 was simultaneously added with an accelerated flow rate so that the silver iodide content was 6.5 mol%, and the silver potential was maintained at -50mV. After 1.5g of thiourea dioxide was added, 132mL of an aqueous solution containing 41.8g of  $\text{AgNO}_3$  and an KBr solution were added by the double jet method over 13 min. The addition of KBr solution was so adjusted that silver potential at the completion of the addition was +40mV. After 2mg of sodium benzenethiosulfonate was added, the temperature was lowered to 40°C, and KBr was added to adjust the silver potential to -40mV. While keeping the temperature at 40°C, a solution containing 14.2g of sodium p-iodoacetamidobenzenesulfonate monohydrate was added, then 57 mL of 0.8M aqueous sodium sulfite solution was added over 1 min at a constant rate, and the pH was controlled to 9.0, thereby iodide ions were made to generate. Two minutes after this, the

temperature was raised to 55°C over 15 min, then pH was lowered to 5.5. Immediately after that, 300mL of an aqueous solution containing 88.5g of AgNO<sub>3</sub> was added over 20 min. During the addition, the silver potential was maintained at -50mV by adding a KBr solution. After washing the mixture with water, gelatin was added, and pH and pAg were adjusted to 6.5 and 8.2, respectively at 40°C. Then, the same processing as for Em-J1 was conducted.

10 (Em-J15)

Em-J15 was prepared in the same manner as Em-J14, except that compound (I-13) of the invention was added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time of chemical sensitization.

15 (Em-J16)

Em-J16 was prepared in the same manner as Em-J15, except that compound (IV-2) of the invention was added at the time of chemical sensitization so that the addition amount thereof was 25 mol% of the sensitizing dyes added.

20 (Em-J17)

Em-J17 was prepared in the same manner as Em-J16, except that compound (IX-2-50) of the invention was added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time of chemical sensitization.

25 (Em-J18)

1200 mL of an aqueous solution containing 0.38g of

phthalated gelatin having a molecular weight of 100,000 and a phthalation rate of 97%, and 0.99g of KBr was vigorously agitated while maintaining the temperature at 60°C and the pH at 2. An aqueous solution  
5 containing 1.96g of  $\text{AgNO}_3$  and an aqueous solution containing 1.97g of KBr and 0.172g of KI were added by the double jet method over a period of 30 sec. After the completion of ripening, 12.8g of trimellitated gelatin whose amino groups were modified with  
10 trimellitic acid, having molecular weight of 100,000 and containing 35  $\mu\text{mol}$ , per gram, of methionine was added. After the pH was adjusted to 5.9, 2.99g of KBr and 6.2g of NaCl were added. 60.7mL of an aqueous solution containing 27.3g of  $\text{AgNO}_3$  and a KBr solution  
15 were added by the double jet method over 35 min. During this period, the silver potential was maintained at -50mV against saturated calomel electrode. An aqueous solution of KBr and an aqueous solution containing 65.6g of  $\text{AgNO}_3$  were added by the double jet  
20 method over a period of 37 min while increasing the flow rate so that the final flow rate was 2.1 times the initial flow rate. During this period, the AgI fine grain emulsion used for the preparation of Em-A1 was simultaneously added with an accelerated flow rate so  
25 that the silver iodide content was 6.5 mol%, and the silver potential was maintained at -50mV. After 1.5g of thiourea dioxide was added, 132mL of an aqueous



solution containing 41.8g of  $\text{AgNO}_3$  and an KBr solution were added by the double jet method over 13 min. The addition of KBr solution was so adjusted that silver potential at the completion of the addition was +40mV.

5 After 2mg of sodium benzenethiosulfonate was added, the temperature was lowered to  $50^\circ\text{C}$ . While maintaining the temperature at  $50^\circ\text{C}$ , 55mL of 0.3% aqueous solution of KI was added over 10 min. Immediately after that, 100mL of an aqueous solution containing 14.2g of  $\text{AgNO}_3$ ,  
10 120mL of an aqueous solution containing 2.1g of NaCl and 4.17g of KBr, and a solution containing 0.0133 mole of AgI fine grains were simultaneously added. During this,  $9.4 \times 10^{-4}$  mole of  $\text{K}_4[\text{RuCN}]_6$  per mol of  $\text{AgNO}_3$  to be added was made present in the reaction mixture.  
15 After that, sensitizing dyes were added in order to stabilize the epitaxial. After washing the mixture with water, gelatin was added, and pH and pAg were adjusted to 6.5 and 8.2, respectively at  $40^\circ\text{C}$ . Then, the same processing as for Em-J1 was conducted.

20 (Em-J19)

Em-J19 was prepared in the same manner as Em-J18, except that compound (I-13) of the invention was added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time of chemical sensitization.

25 (Em-J20)

Em-J20 was prepared in the same manner as Em-J19, except that compound (IV-2) of the invention was added

at the time of chemical sensitization so that the addition amount thereof was 25 mol% of the sensitizing dyes added.

(Em-J21)

5           Em-J21 was prepared in the same manner as Em-J20, except that compound (IX-2-50) of the invention was added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time of chemical sensitization.

(Em-J22)

10           1200 mL of an aqueous solution containing 0.38g of phthalated gelatin having a molecular weight of 100,000 and a phthalation rate of 97%, and 0.99g of KBr was vigorously agitated while maintaining the temperature at 60°C and the pH at 2. An aqueous solution  
15           containing 1.96g of  $\text{AgNO}_3$  and an aqueous solution containing 1.97g of KBr and 0.172g of KI were added by the double jet method over a period of 30 sec. After the completion of ripening, 12.8g of trimellitated gelatin whose amino groups were modified with  
20           trimellitic acid, having molecular weight of 100,000 and containing 35  $\mu\text{mol}$ , per gram, of methionine was added. After the pH was adjusted to 5.9, 2.99g of KBr and 6.2g of NaCl were added. Into a mixing apparatus situated outside the reaction vessel, 762mL of an  
25           aqueous solution containing 92.9g of  $\text{AgNO}_3$  and 762mL of an aqueous solution containing 60.8g of KBr, 5.9g of KI, and 38.1g of gelatin having a molecular weight of

20,000 were simultaneously added thereby preparing a AgBrI fine grain emulsion (average grain size:  $0.015\mu$  m). While preparing the fine grain emulsion, the fine emulsion was added to the reaction vessel over 90 min.

5 At this time, silver potential was maintained at -30mV against saturated calomel electrode. After 1.5g of thiourea dioxide was added, 132mL of an aqueous solution containing 41.8g of  $\text{AgNO}_3$  and an KBr solution were added by the double jet method over 13 min. The

10 addition of KBr solution was so adjusted that silver potential at the completion of the addition was +40mV. After 2mg of sodium benzenethiosulfonate was added, the temperature was lowered to  $50^\circ\text{C}$ . Then the temperature was lowered to  $40^\circ\text{C}$ , KBr was added to adjust the silver

15 potential to -40mV. While keeping the temperature at  $40^\circ\text{C}$ , a solution containing 14.2g of sodium p-iodoacetamidobenzenesulfonate monohydrate was added, then 57 mL of 0.8M aqueous sodium sulfite solution was added over 1 min at a constant rate, and the pH was

20 controlled to 9.0, thereby iodide ions were made to generate. Two minutes after this, the temperature was raised to  $55^\circ\text{C}$  over 15 min, then pH was lowered to 5.5. Immediately after that, 300mL of an aqueous solution containing 88.5g of  $\text{AgNO}_3$  was added over 20 min.

25 During the addition, the silver potential was maintained at -50mV by adding a KBr solution. After washing the mixture with water, gelatin comprising, in

an amount of 30%, components each having a molecular weight measured according to the PAGI method of 280,000 or more was added, and pH and pAg were adjusted to 6.5 and 8.2, respectively at 40°C. Then, the same processing as for Em-J1 was conducted.

(Em-J23)

Em-J23 was prepared in the same manner as Em-J22, except that compound (I-13) of the invention was added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time of chemical sensitization.

(Em-J24)

Em-J24 was prepared in the same manner as Em-J23, except that compound (IV-2) of the invention was added at the time of chemical sensitization so that the addition amount thereof was 25 mol% of the sensitizing dyes added.

(Em-J25)

Em-J25 was prepared in the same manner as Em-J24, except that each of compounds (I-13) and (IX-2-50) of the invention was added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time of chemical sensitization.

Table 1

Emulsion No.	Compound No. added to emulsion	Content with respect to sensitizing dye (mol%)
Em-J1	none	-
Em-J4	IV-2	2
Em-J5	IV-2	5
Em-J6	IV-2	10
Em-J7	IV-2	25
Em-J8	IV-2	50
Em-J9	IV-2	2
Em-J10	IV-2	5
Em-J11	IV-2	10
Em-J12	IV-2	25
Em-J13	IV-2	50

(Em-K: Emulsion for a medium-speed red sensitive layer)

5           1200 mL of an aqueous solution containing 4.9g of low molecular weight gelatin having a molecular weight of 15,000 and 5.3g of KBr was vigorously agitated while maintaining the temperature at 60°C. 27mL of an aqueous solution containing 8.75g of AgNO<sub>3</sub> and 36mL of an aqueous solution containing 6.45g of KBr were added by the double jet method over 1 min. After the temperature was raised to 77°C, 21mL of an aqueous solution containing 6.9g of AgNO<sub>3</sub> was added over 2.5 min. 26g of NH<sub>4</sub>NO<sub>3</sub>, 56mL of 1N NaOH solution were sequentially added, then, ripened the mixture. After completion of ripening, pH was adjusted to 4.8. 438mL of an aqueous solution containing 141g of AgNO<sub>3</sub> and 458mL of an aqueous solution containing 102.6g of KBr

10

15

were added by the double jet method while the flow rate was accelerated so that the final flow rate was 4 times the initial flow rate. After the temperature was raised to 55°C, 240mL of an aqueous solution containing 7.1g of AgNO<sub>3</sub> and an aqueous solution containing 6.46g of KI were added by the double jet method over 5 min. After 7.1g of KBr was added, 4mg of sodium benzenethiosulfonate and 0.05mg of K<sub>2</sub>IrCl<sub>6</sub> were added. 177mL of an aqueous solution containing 57.2 g of AgNO<sub>3</sub> and 223mL of an aqueous solution containing 40.2g of KBr were added by the double jet method over 8 min. The thus obtained mixture was washed with water and chemically sensitized by almost the same manner as for Em-J1.

(Em-L: Emulsion for a medium-speed red sensitive layer)

Em-L was prepared by almost the same manner as Em-K, except that the temperature during nucleation was changed to 42°C.

(Em-M, -N, and -O)

Em-M, -N, and -O were prepared by almost the same manner as Em-H or Em-I, but the chemical sensitization was performed by almost the same manner as in Em-J.

(Em-P1)

Em-P1 was prepared in the same manner as Em-J1, except that the sensitizing dyes were changed to sensitizing dyes 15, 16 and 17 to perform optimal

chemical sensitization.

(Em-P2)

Em-P2 was prepared in the same manner as Em-P1, except that compound (I-13) of the invention was added  
5 in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time of chemical sensitization.

(Em-P3)

Em-P3 was prepared in the same manner as Em-P1, except that compound (IX-2-50) of the invention was  
10 added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time of chemical sensitization.

(Em-P4)

Em-P4 was prepared in the same manner as Em-J14, except that the sensitizing dyes were changed to  
15 sensitizing dyes 15, 16 and 17, to perform optimal chemical sensitization.

(Em-P5)

Em-P5 was prepared in the same manner as Em-P4, except that compound (I-13) of the invention was added  
20 in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time of chemical sensitization.

(Em-P6)

Em-P6 was prepared in the same manner as Em-P5, except that compound (IX-2-50) of the invention was  
25 added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time of chemical sensitization.

(Em-P7)

Em-P7 was prepared in the same manner as Em-J18, except that the sensitizing dyes were changed to sensitizing dyes 15, 16 and 17, to perform optimal chemical sensitization.

5 (Em-P8)

Em-P8 was prepared in the same manner as Em-P7, except that compound (I-13) of the invention was added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time of chemical sensitization.

10 (Em-P9)

Em-P9 was prepared in the same manner as Em-P8, except that compound (IX-2-50) of the invention was added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time of chemical sensitization.

15 (Em-P10)

Em-P10 was prepared in the same manner as Em-J22, except that the sensitizing dyes were changed to sensitizing dyes 15, 16 and 17, to perform optimal chemical sensitization.

20 (Em-P11)

Em-P11 was prepared in the same manner as Em-P10, except that compound (I-13) of the invention was added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time of chemical sensitization.

25 (Em-P12)

Em-P12 was prepared in the same manner as Em-P11, except that compound (IX-2-50) of the invention was



added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time of chemical sensitization.

The characteristics of the thus obtained silver halide emulsions Em-A1 to Em-P12 are set forth in Table

5 2.

Table 2  
Grain characteristics of silver halide emulsions Em-A1 to P12

Emulsion No.	E.S.D. $\mu\text{m}$	P.A.D. $\mu\text{m}$	Aspect ratio	I content mol%	Surface index of main planes	Cl content mol%
Em-A1 to A3	1.7	3.15	9.5	6.1	(111)	0
Em-A4 to A6	1.7	3.25	10.5	6.1	(111)	0
Em-A7 to A9	1.7	3.2	10	6.1	(111)	0
Em-A10 to A12	1.7	3.25	10.5	6.1	(111)	0
Em-A13 to A15	1.7	3.4	12	6.1	(111)	0
Em-B	1.0	2.0	12.2	10.0	(111)	0
Em-C	0.7	-	1	4.0	(111)	1.0
Em-D	0.4	0.53	3.5	4.1	(111)	2.0
Em-E	1.1	2.63	20.6	6.7	(111)	0
Em-F	1.2	2.74	18	6.9	(111)	0
Em-G	0.9	1.98	15.9	6.1	(111)	0
Em-H	0.7	1.22	8	6.0	(111)	2.0
Em-I	0.4	0.63	6	6.0	(111)	2.0
Em-J1 to J13	1.3	3.18	22	3.5	(111)	0
Em-J14 to J17	1.3	3.18	22	3.5	(111)	0
Em-J18 to J21	1.3	3.22	23	3.5	(111)	0
Em-J22 to J25	1.3	3.28	24	3.5	(111)	0
Em-K	1.0	2.37	20	4.0	(111)	0
Em-L	0.8	1.86	19	3.6	(111)	0
Em-M	0.6	1.09	8.9	2.9	(111)	2.0
Em-N	0.4	0.63	6	2.0	(111)	2.0
Em-O	0.3	0.38	3	1.0	(111)	2.0
Em-P1 to P3	1.3	3.18	22	3.5	(111)	0
Em-P4 to P6	1.3	3.18	22	3.5	(111)	0
Em-P7 to P9	1.3	3.22	23	3.5	(111)	0
Em-P10 to P12	1.3	3.28	24	3.5	(111)	0

E.S.D. = Equivalent sphere diameter

P.A.D. = Projected area diameter

The outline of the preparation formula of an emulsified dispersion is set forth below.

Into 10% gelatin solution, a solution of a coupler dissolved in ethyl acetate, a high boiling organic solvent, and a surfactant were added and mixed using a homogenizer (produced by NIHONSEIKI), thereby emulsify the mixture to obtain a emulsified dispersion.

1) Support

A support used in this example was formed as follows.

100 parts by weight of a polyethylene-2,6-naphthalate polymer and 2 parts by weight of Tinuvin P.326 (manufactured by Ciba-Geigy Co.) as an ultraviolet absorbent were dried, melted at 300°C, and extruded from a T-die. The resultant material was longitudinally oriented by 3.3 times at 140°C, laterally oriented by 3.3 times at 130°C, and thermally fixed at 250°C for 6 sec, thereby obtaining a 90 µm thick PEN (polyethylenenaphthalate) film. Note that proper amounts of blue, magenta, and yellow dyes (I-1, I-4, I-6, I-24, I-26, I-27, and II-5 described in Journal of Technical Disclosure No. 94-6023) were added to this PEN film. The PEN film was wound around a stainless steel core 20 cm in diameter and given a thermal history of 110°C and 48 hr, manufacturing a support with a high resistance to curling.

2) Coating of undercoat layer

The two surfaces of the above support were subjected to corona discharge, UV discharge, and glow discharge. After that, each surface of the support was coated with an undercoat solution ( $10 \text{ mL/m}^2$ , by using a bar coater) consisting of  $0.1 \text{ g/m}^2$  of gelatin,  $0.01 \text{ g/m}^2$  of sodium  $\alpha$ -sulfodi-2-ethylhexylsuccinate,  $0.04 \text{ g/m}^2$  of salicylic acid,  $0.2 \text{ g/m}^2$  of p-chlorophenol,  $0.012 \text{ g/m}^2$  of  $(\text{CH}_2=\text{CHSO}_2\text{CH}_2\text{CH}_2\text{NHCO})_2\text{CH}_2$ , and  $0.02 \text{ g/m}^2$  of a polyamido-epichlorohydrin polycondensation product, thereby forming an undercoat layer on a side at a high temperature upon orientation. Drying was performed at  $115^\circ\text{C}$  for 6 min (all rollers and conveyors in the drying zone were at  $115^\circ\text{C}$ ).

3) Coating of back layers

One surface of the undercoated support was coated with an antistatic layer, magnetic recording layer, and slip layer having the following compositions as back layers.

3-1) Coating of antistatic layer

The surface was coated with  $0.2 \text{ g/m}^2$  of a dispersion (secondary aggregation grain size = about  $0.08 \mu\text{m}$ ) of a fine-grain powder, having a specific resistance of  $5 \Omega \cdot \text{cm}$ , of a tin oxide-antimony oxide composite material with an average grain size of  $0.005 \mu\text{m}$ , together with  $0.05 \text{ g/m}^2$  of gelatin,  $0.02 \text{ g/m}^2$  of  $(\text{CH}_2=\text{CHSO}_2\text{CH}_2\text{CH}_2\text{NHCO})_2\text{CH}_2$ ,  $0.005 \text{ g/m}^2$  of

polyoxyethylene-p-nonylphenol (polymerization degree 10), and resorcin.

### 3-2) Coating of magnetic recording layer

A bar coater was used to coat the surface with  
5 0.06 g/m<sup>2</sup> of cobalt- $\gamma$ -iron oxide (specific area  
43 m<sup>2</sup>/g, major axis 0.14  $\mu$ m, minor axis 0.03  $\mu$ m,  
saturation magnetization 89 Am<sup>2</sup>/kg, Fe<sup>+2</sup>/Fe<sup>+3</sup> = 6/94,  
the surface was treated with 2 wt% of iron oxide  
by aluminum oxide silicon oxide) coated with  
10 3-poly(polymerization degree 15)oxyethylene-  
propyloxytrimethoxysilane (15 wt%), together with  
1.2 g/m<sup>2</sup> of diacetylcellulose (iron oxide was dispersed  
by an open kneader and sand mill), by using 0.3 g/m<sup>2</sup>  
of C<sub>2</sub>H<sub>5</sub>C(CH<sub>2</sub>CONH-C<sub>6</sub>H<sub>3</sub>(CH<sub>3</sub>)NCO)<sub>3</sub> as a hardener and  
15 acetone, methylethylketone, and cyclohexane as  
solvents, thereby forming a 1.2  $\mu$ m thick magnetic  
recording layer. 10 mg/m<sup>2</sup> of silica grains (0.3  $\mu$ m)  
were added as a matting agent, and 10 mg/m<sup>2</sup> of aluminum  
oxide (0.15  $\mu$ m) coated with 3-poly(polymerization  
20 degree 15)oxyethylene-propyloxytrimethoxysilane  
(15 wt%) were added as a polishing agent. Drying was  
performed at 115°C for 6 min (all rollers and conveyors  
in the drying zone were at 115°C). The color density  
increase of D<sup>B</sup> of the magnetic recording layer  
25 measured by an X-light (blue filter) was about 0.1.  
The saturation magnetization moment, coercive force,  
and squareness ratio of the magnetic recording layer

were  $4.2 \text{ Am}^2/\text{kg}$ ,  $7.3 \times 10^4 \text{ A/m}$ , and 65%, respectively.

### 3-3) Preparation of slip layer

The surface was then coated with diacetylcellulose ( $25 \text{ mg/m}^2$ ) and a mixture of  $\text{C}_6\text{H}_{13}\text{CH}(\text{OH})\text{C}_{10}\text{H}_{20}\text{COOC}_{40}\text{H}_{81}$  (compound a,  $6 \text{ mg/m}^2$ )/ $\text{C}_{50}\text{H}_{101}\text{O}(\text{CH}_2\text{CH}_2\text{O})_{16}\text{H}$  (compound b,  $9 \text{ mg/m}^2$ ). Note that this mixture was melted in xylene/propylenemonomethylether (1/1) at  $105^\circ\text{C}$  and poured and dispersed in propylenemonomethylether (tenfold amount) at room temperature. After that, the resultant mixture was formed into a dispersion (average grain size  $0.01 \mu\text{m}$ ) in acetone before being added.  $15 \text{ mg/m}^2$  of silica grains ( $0.3 \mu\text{m}$ ) were added as a matting agent, and  $15 \text{ mg/m}^2$  of aluminum oxide ( $0.15 \mu\text{m}$ ) coated with 3-poly(polymerization degree 15)oxyethylene-propyloxytrimethoxysilane (15 wt%) were added as a polishing agent. Drying was performed at  $115^\circ\text{C}$  for 6 min (all rollers and conveyors in the drying zone were at  $115^\circ\text{C}$ ). The resultant slip layer was found to have excellent characteristics; the coefficient of kinetic friction was 0.06 (5 mm $\varnothing$  stainless steel hard sphere, load 100g, speed 6 cm/min), and the coefficient of static friction was 0.07 (clip method). The coefficient of kinetic friction between an emulsion surface (to be described later) and the slip layer also was excellent, 0.12.

### 4) Coating of sensitive layers

The surface of the support on the side away from

the back layers formed as above was coated with a plurality of layers having the following compositions to form a sample as a color negative sensitized material. For the preparation of the samples,

5 emulsions, emulsified dispersions and couplers set forth in Tables 3, 4, and 5 were used. Regarding emulsions, couplers, high-boiling organic solvents, and surfactants, the substitution was conducted in the same amount. When the substitution was conducted using  
10 plural kinds of the emulsions, couplers, high-boiling organic solvents, or surfactants, the substitution was conducted so that the total amount of the plural kinds was the same amount. Specifically, when one coupler is substituted with two kinds of couplers, the amount of  
15 each one of the two coupler is  $1/2$  the one coupler to be substituted. Similarly, when one emulsion is replaced with three kinds of emulsions, the amount of each one of the three emulsions is  $1/3$  the one emulsion to be substituted.

20 (Compositions of sensitive layers)

The main ingredients used in the individual layers are classified as follows, however, the use thereof are not limited to those specified below.

ExC: Cyan coupler      UV : Ultraviolet absorbent

25 ExM: Magenta coupler    HBS: High-boiling organic solvent

ExY: Yellow coupler    H : Gelatin hardener

(In the following description, practical compounds

have numbers attached to their symbols. Formulas of these compounds will be presented later.)

The number corresponding to each component indicates the coating amount in units of g/m<sup>2</sup>. The coating amount of a silver halide is indicated by the amount of silver.

1st layer (1st antihalation layer)

	Black colloidal silver	silver	0.155
	AgBrI (2) of surface fogged emulsion		
10	having 0.07 $\mu$ m	silver	0.01
	Gelatin		0.87
	ExC-1		0.002
	ExC-3		0.002
	Cpd-2		0.001
15	HBS-1		0.004
	HBS-2		0.002

2nd layer (2nd antihalation layer)

	Black colloidal silver	silver	0.066
	Gelatin		0.407
20	ExM-1		0.050
	ExF-1		$2.0 \times 10^{-3}$
	HBS-1		0.074
	Solid disperse dye ExF-2		0.015
	Solid disperse dye ExF-3		0.020

25 3rd layer (Interlayer)

	AgBrI (2) emulsion having 0.07 $\mu$ m		
		silver	0.020



	ExC-2		0.022
	Polyethylacrylate latex		0.085
	Gelatin		0.294
	4th layer (Low-speed red-sensitive emulsion layer)		
5	Silver iodobromide emulsion M	silver	0.065
	Silver iodobromide emulsion N	silver	0.100
	Silver iodobromide emulsion O	silver	0.158
	ExC-1		0.109
	ExC-3		0.044
10	ExC-4		0.072
	ExC-5		0.011
	ExC-6		0.003
	Cpd-2		0.025
	Cpd-4		0.025
15	HBS-1		0.17
	Gelatin		0.80
	5th layer (Medium-speed red-sensitive emulsion layer)		
	Silver iodobromide emulsion K	silver	0.21
	Silver iodobromide emulsion L	silver	0.62
20	ExC-1		0.14
	ExC-2		0.026
	ExC-3		0.020
	ExC-4		0.12
	ExC-5		0.016
25	ExC-6		0.007
	Cpd-2		0.036
	Cpd-4		0.028

	HBS-1	0.16
	Gelatin	1.18
	6th layer (High-speed red-sensitive emulsion layer)	
	Silver iodobromide emulsion J silver	1.67
5	ExC-1	0.18
	ExC-3	0.07
	ExC-6	0.047
	Cpd-2	0.046
	Cpd-4	0.077
10	HBS-1	0.25
	HBS-2	0.12
	Gelatin	2.12
	7th layer (Interlayer)	
	Cpd-1	0.089
15	Solid disperse dye ExF-4	0.030
	HBS-1	0.050
	Polyethylacrylate latex	0.83
	Gelatin	0.84
	8th layer (Interimage donating layer (layer for donating interimage effect to red-sensitive layer))	
20	Silver iodobromide emulsion E silver	0.560
	Cpd-4	0.030
	ExM-2	0.096
25	ExM-3	0.028
	ExY-1	0.031
	ExG-1	0.006
	HBS-1	0.085

	HBS-3	0.003
	Gelatin	0.58
	9th layer (Low-speed green-sensitive emulsion layer)	
	Silver iodobromide emulsion G silver	0.39
5	Silver iodobromide emulsion H silver	0.28
	Silver iodobromide emulsion I silver	0.35
	ExM-2	0.36
	ExM-3	0.045
	ExG-1	0.005
10	HBS-1	0.28
	HBS-3	0.01
	HBS-4	0.27
	Gelatin	1.39
	10th layer (Medium-speed green-sensitive emulsion layer)	
15	Silver iodobromide emulsion F silver	0.20
	Silver iodobromide emulsion G silver	0.25
	ExC-6	0.009
	ExM-2	0.031
20	ExM-3	0.029
	ExY-1	0.006
	ExM-4	0.028
	ExG-1	0.005
	HBS-1	0.064
25	HBS-3	$2.1 \times 10^{-3}$
	Gelatin	0.44
	11th layer (High-speed green-sensitive emulsion layer)	

	Emulsion Em-P1 of Example 1	silver	1.200
	ExC-6		0.004
	ExM-1		0.016
	ExM-3		0.036
5	ExM-4		0.020
	ExM-5		0.004
	ExY-5		0.008
	ExM-2		0.013
	Cpd-4		0.007
10	HBS-1		0.18
	Polyethylacrylate latex		0.099
	Gelatin		1.11
	12th layer (Yellow filter layer)		
	Yellow colloidal silver	silver	0.047
15	Cpd-1		0.16
	ExF-5		0.010
	Solid disperse dye ExF-6		0.010
	HBS-1		0.082
	Gelatin		1.057
20	13th layer (Low-speed blue-sensitive emulsion layer)		
	Silver iodobromide emulsion B	silver	0.18
	Silver iodobromide emulsion C	silver	0.20
	Silver iodobromide emulsion D	silver	0.07
	ExC-1		0.041
25	ExC-8		0.012
	ExY-1		0.035
	ExY-2		0.71

	ExY-3	0.10
	ExY-4	0.005
	Cpd-2	0.10
	Cpd-3	$4.0 \times 10^{-3}$
5	HBS-1	0.24
	Gelatin	1.41
	14th layer (High-speed blue-sensitive emulsion layer)	
	Silver iodobromide emulsion A	silver 0.75
	ExC-1	0.013
10	ExY-2	0.31
	ExY-3	0.05
	ExY-6	0.062
	Cpd-2	0.075
	Cpd-3	$1.0 \times 10^{-3}$
15	HBS-1	0.10
	Gelatin	0.91
	15th layer (1st protective layer)	
	AgBrI (2) emulsion having $0.07 \mu\text{m}$	
		silver 0.30
20	UV-1	0.21
	UV-2	0.13
	UV-3	0.20
	UV-4	0.025
	F-11	0.009
25	F-18	0.005
	F-19	0.005
	HBS-1	0.12

	HBS-4	$5.0 \times 10^{-2}$
	Gelatin	2.3
	16th layer (2nd protective layer)	
	H-1	0.40
5	B-1 (diameter $1.7 \mu\text{m}$ )	$5.0 \times 10^{-2}$
	B-2 (diameter $1.7 \mu\text{m}$ )	0.15
	B-3	0.05
	S-1	0.20
	Gelatin	0.75

10 In addition to the above components, to improve the storage stability, processability, resistance to pressure, antiseptic and mildewproofing properties, antistatic properties, and coating properties, the individual layers contained B-4 to B-6, F-1 to F-17, 15 iron salt, lead salt, gold salt, platinum salt, palladium salt, iridium salt, ruthenium salt, and rhodium salt. Additionally, a sample was manufactured by adding  $8.5 \times 10^{-3}\text{g}$  and  $7.9 \times 10^{-3}\text{g}$ , per mol of 20 a silver halide, of calcium in the form of an aqueous calcium nitrate solution to the coating solutions of the 8th and 11th layers, respectively.

Preparation of dispersions of organic solid disperse dyes

ExF-3 was dispersed by the following method.

25 That is, 21.7 mL of water, 3 mL of a 5% aqueous solution of p-octylphenoxyethoxyethanesulfonic acid soda, and 0.5g of a 5% aqueous solution of

p-octylphenoxypolyoxyethyleneether (polymerization degree 10) were placed in a 700 mL pot mill, and 5.0g of the dye ExF-3 and 500 mL of zirconium oxide beads (diameter 1 mm) were added to the mill. The contents  
5 were dispersed for 2 hr. This dispersion was done by using a BO type oscillating ball mill manufactured by Chuo Koki K.K. After the dispersion, the dispersion was extracted from the mill and added to 8g of a 12.5% aqueous solution of gelatin. The beads were filtered  
10 away to obtain a gelatin dispersion of the dye. The average grain size of the fine dye grains was 0.44  $\mu\text{m}$ .

Following the same procedure as above, solid dispersions ExF-4 was obtained. The average grain sizes of the fine dye grains was 0.45. ExF-2 was  
15 dispersed by a microprecipitation dispersion method described in Example 1 of EP549,489A. The average grain size was found to be 0.06  $\mu\text{m}$ .

A solid dispersion ExF-6 was dispersed by the following method.

20 4000 g of water and 376g of a 3% solution of W-2 were added to 2,800g of a wet cake of ExF-6 containing 18% of water, and the resultant material was stirred to form a slurry of ExF-6 having a concentration of 32%. Next, ULTRA VISCO MILL (UVM-2) manufactured by Imex  
25 K.K. was filled with 1,700 mL of zirconia beads having an average grain size of 0.5 mm. The slurry was milled by passing through the mill for 8 hr at a peripheral

speed of about 10 m/sec and a discharge amount of 0.5 L/min.

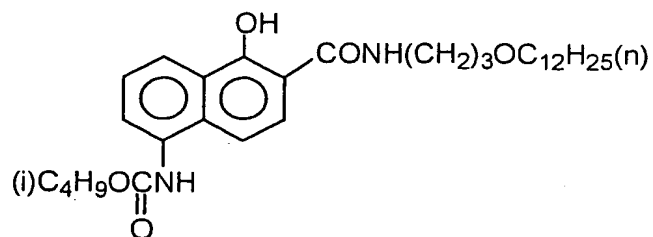
The compounds used in the formation of each layer are as follows.

5

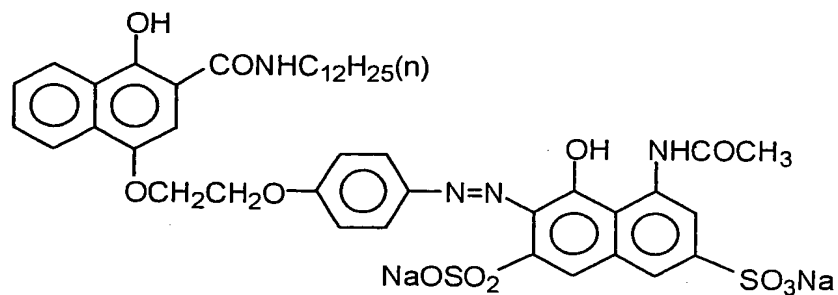
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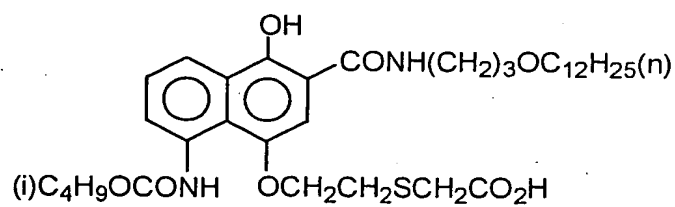
ExC-1



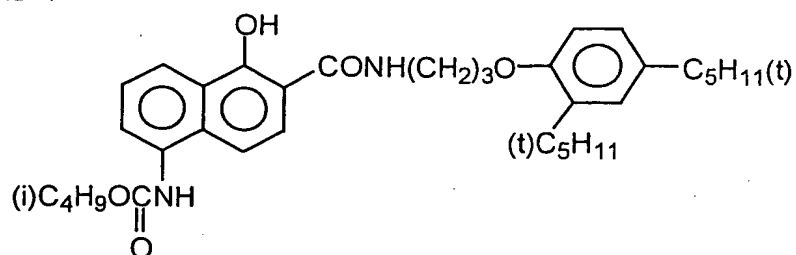
ExC-2



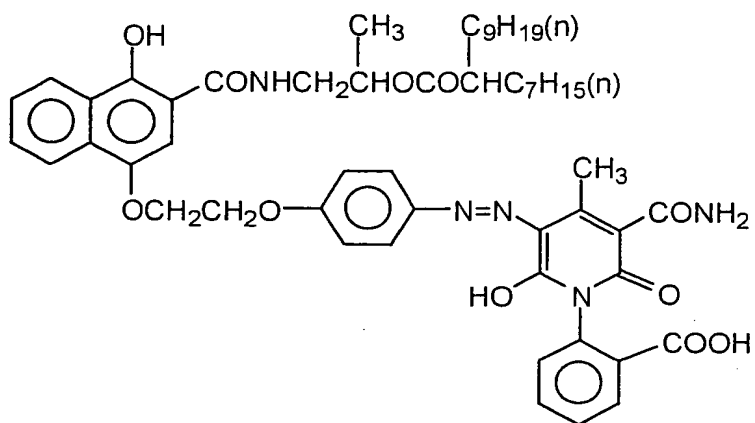
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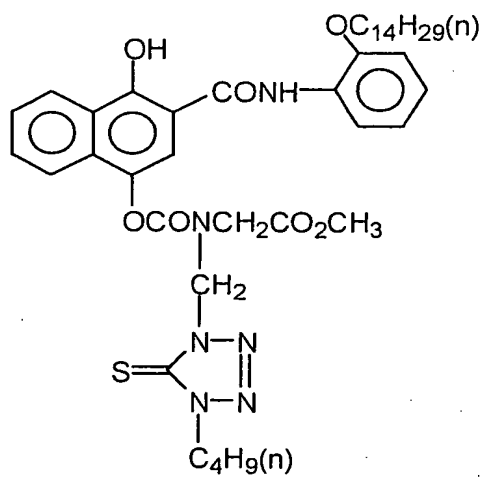
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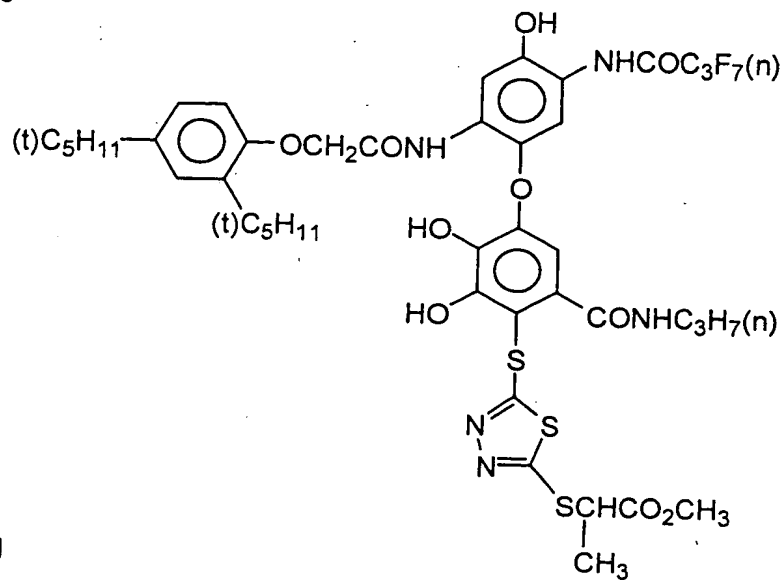
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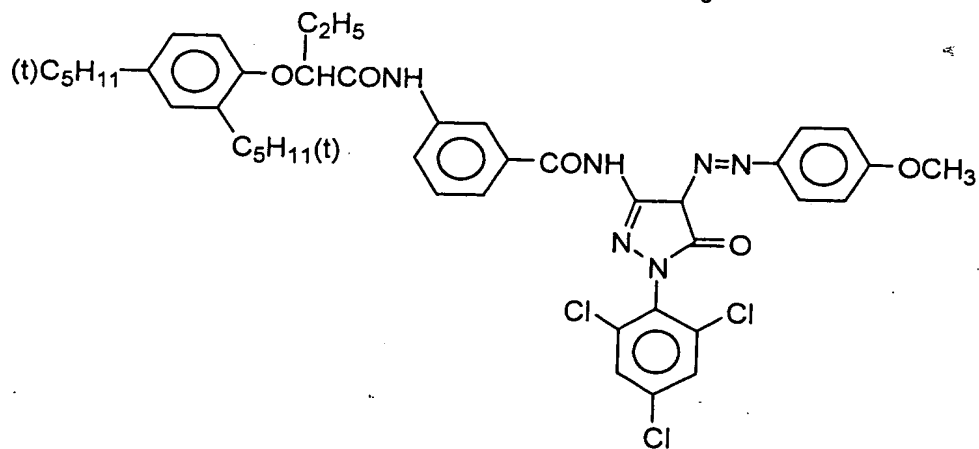
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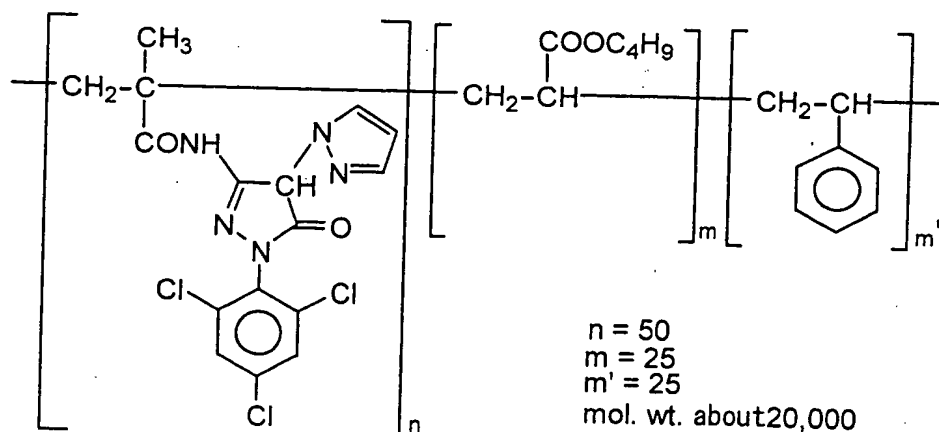
ExC-8



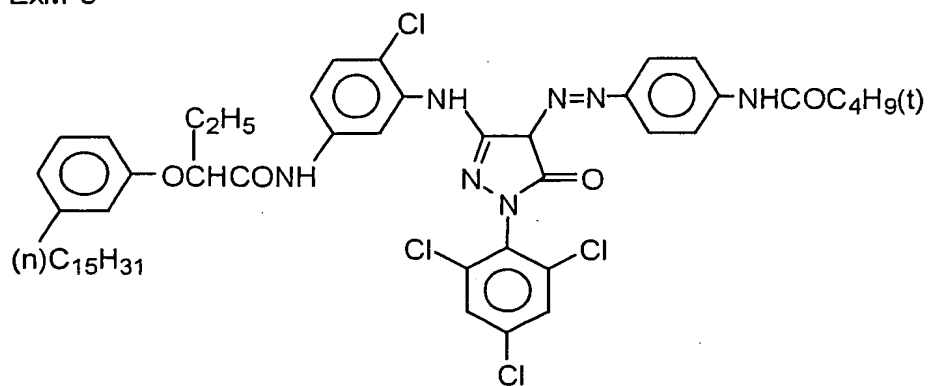
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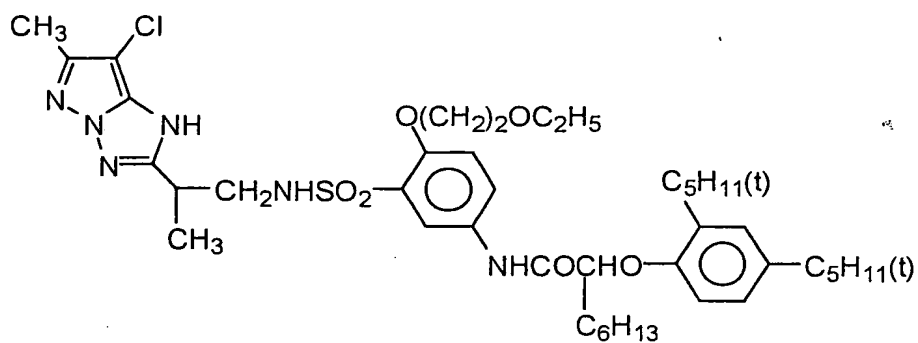
ExM-2



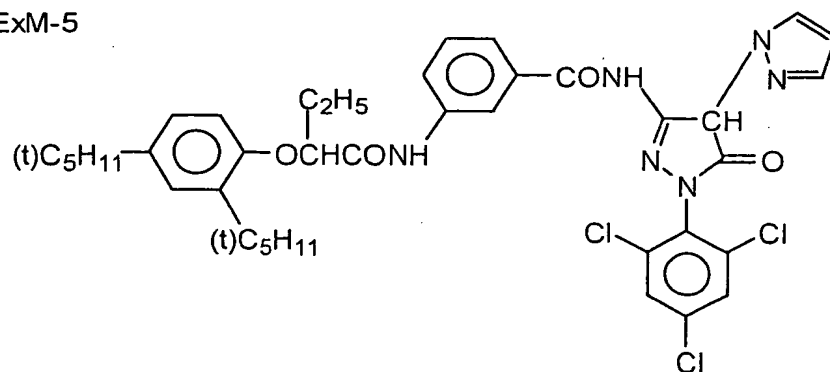
ExM-3



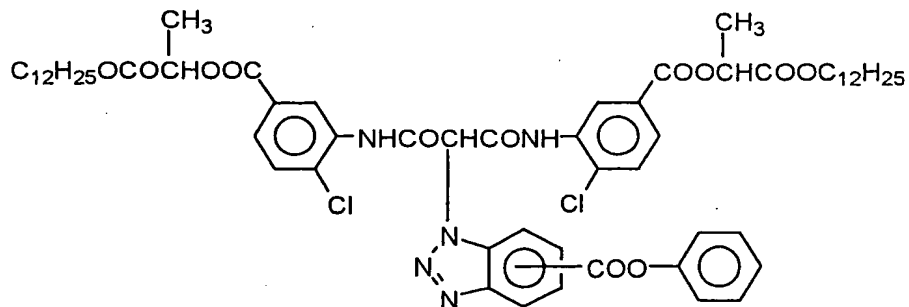
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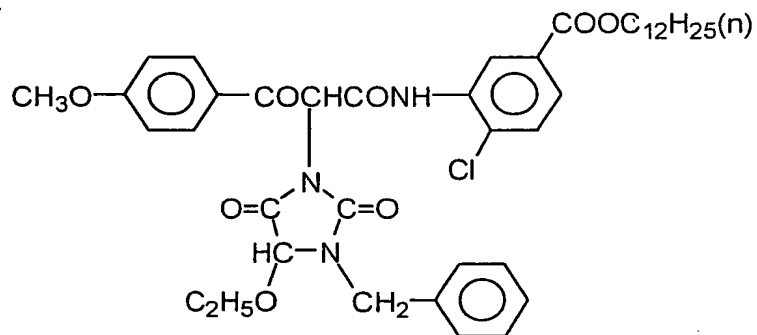
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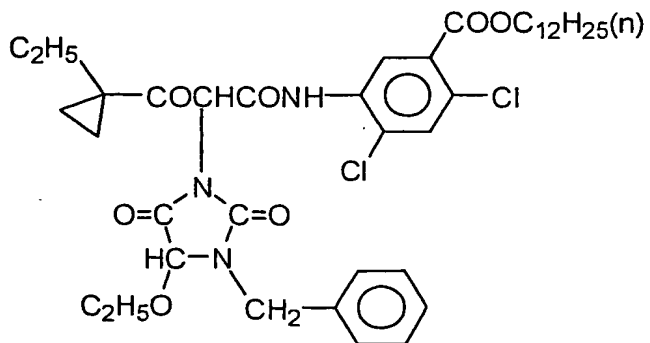
ExY-1



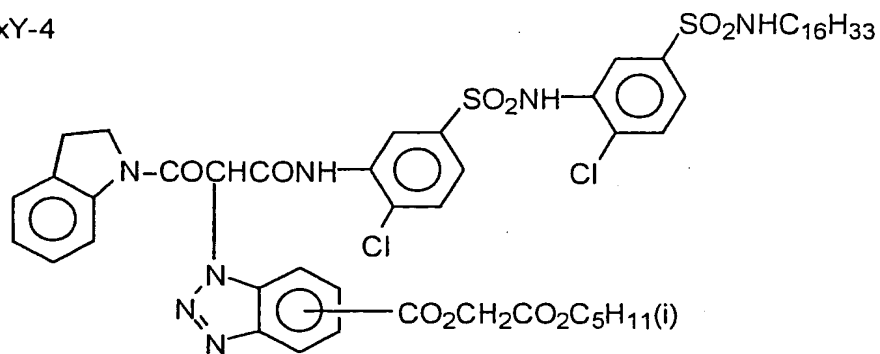
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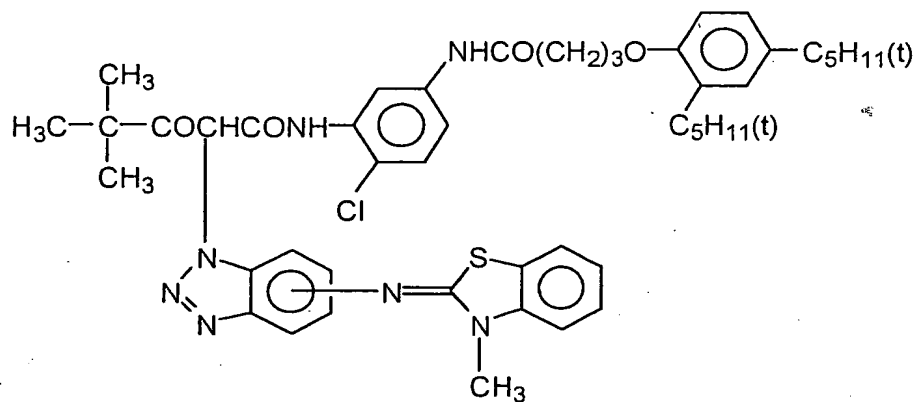
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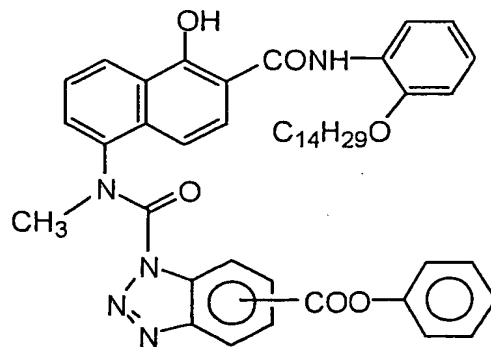
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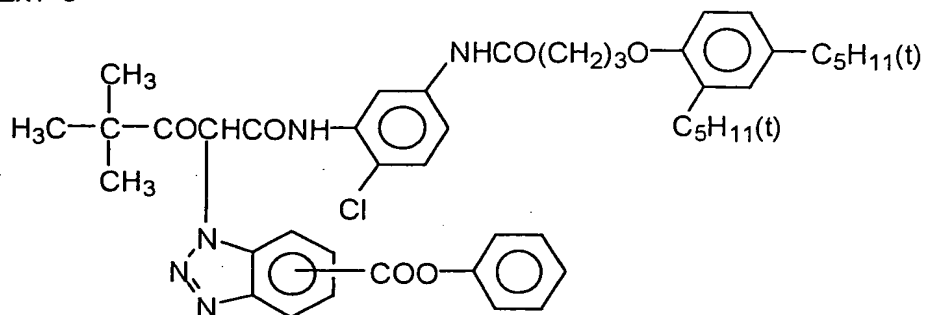
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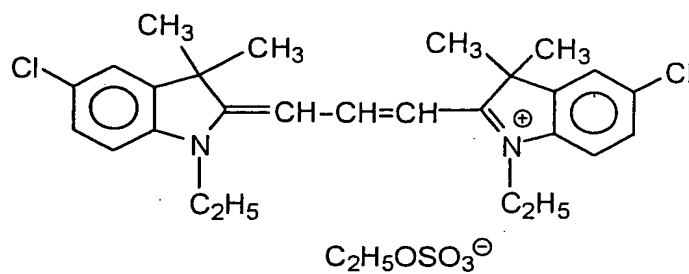
ExG-1



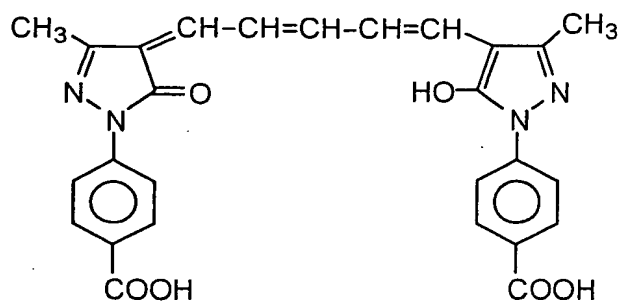
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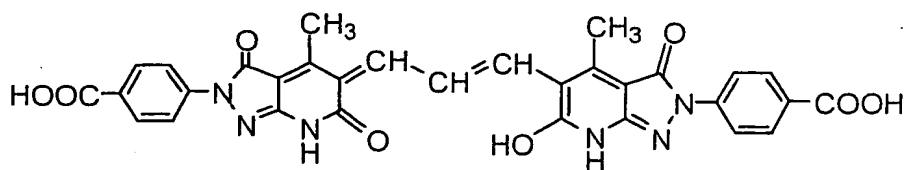
ExF-1



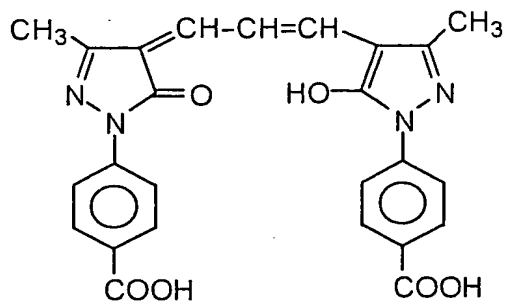
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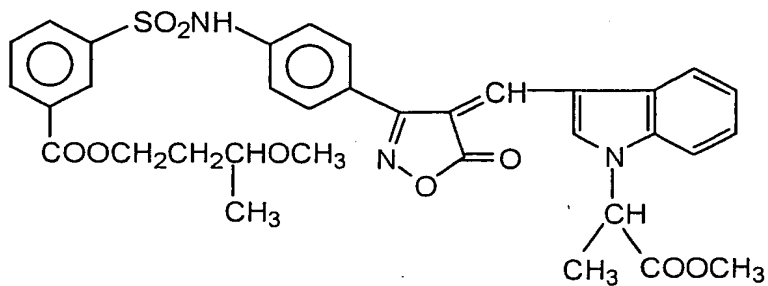
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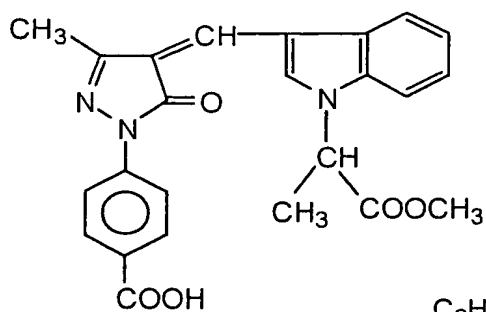
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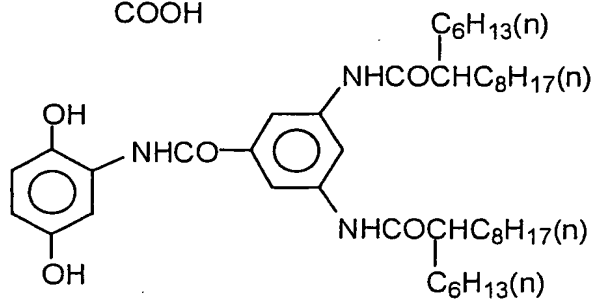
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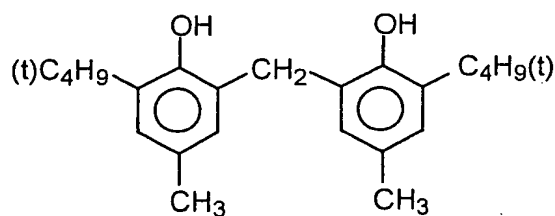
ExF-6



Cpd-1

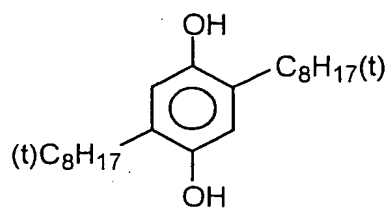


Cpd-2

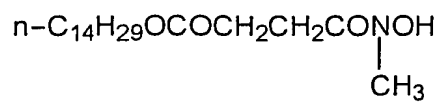




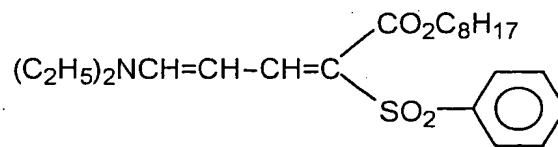
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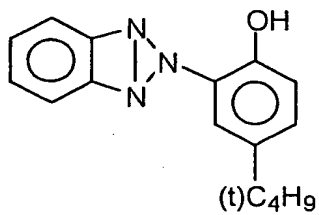
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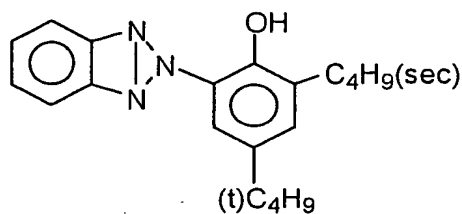
UV-1



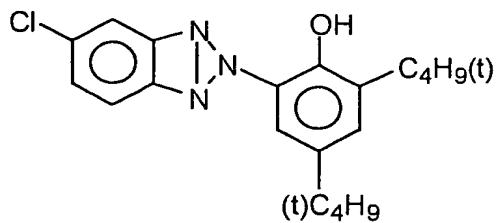
UV-2



UV-3

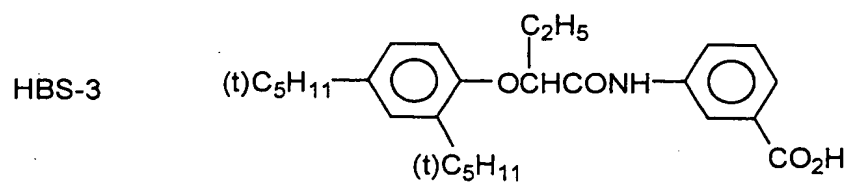


UV-4



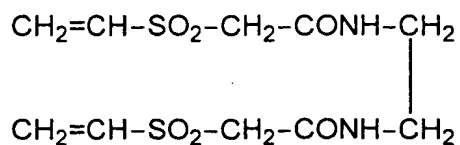
HBS-1      Tricresyl phostate

HBS-2      Di-n-butylphthalate

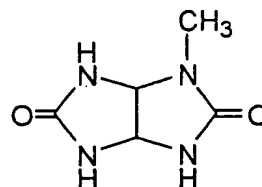


HBS-4      Tri (2-ethylhexyl) phosphate

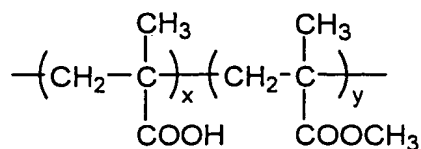
H-1



S-1



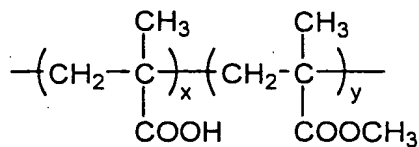
B-1



x/y=10/90 (Weight ratio)

Average mol. wt. : about 35,000

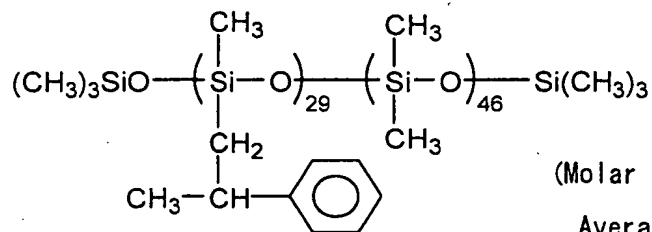
B-2



x/y=40/60 (Weight ratio)

Average mol. wt. : about 20,000

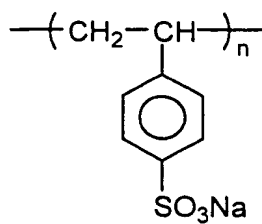
B-3



(Molar ratio)

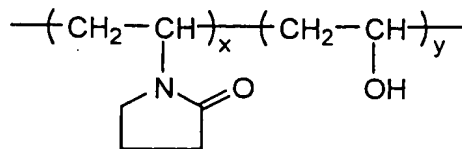
Average mol. wt. : about 8,000

B-4



Average mol. wt. : about 750,000

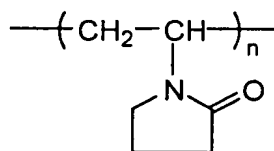
B-5



x/y=70/30 (Weight ratio)

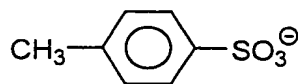
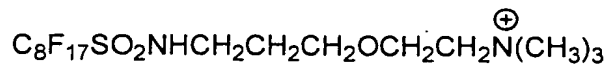
Average mol. wt. : about 17,000

B-6

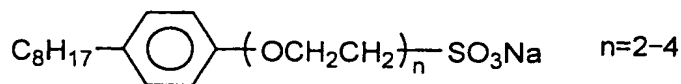


Average mol. wt. : about 10,000

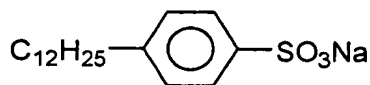
W-1



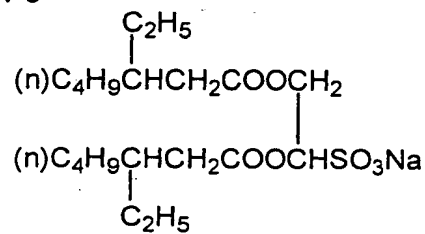
W-2



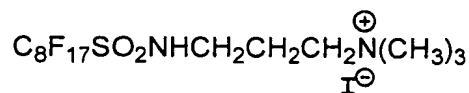
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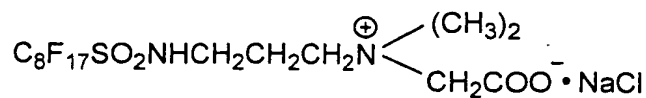
W-5



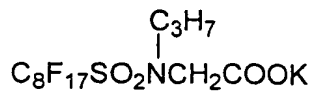
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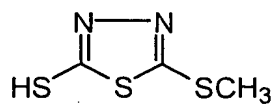
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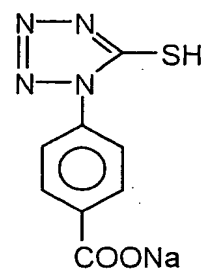
W-8



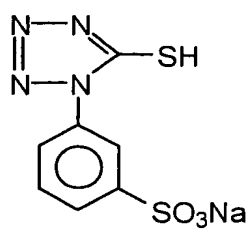
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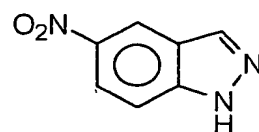
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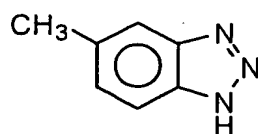
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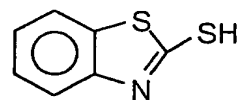
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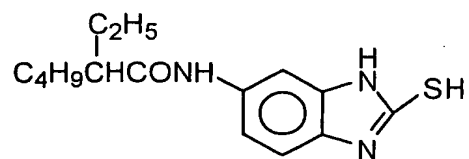
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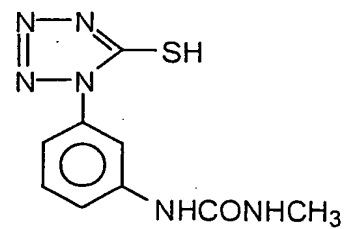
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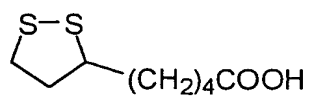
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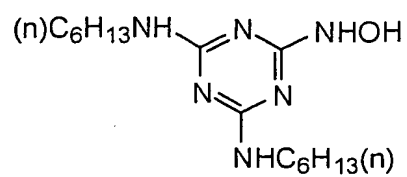
F-8



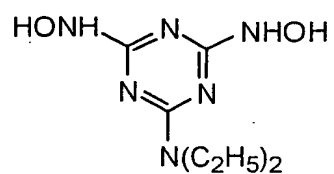
F-9



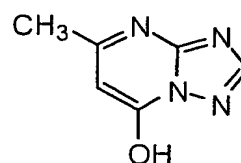
F-10



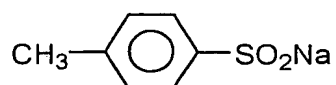
F-11



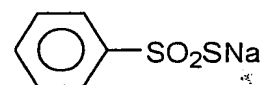
F-12



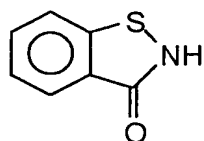
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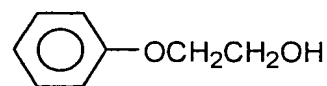
F-14



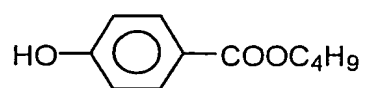
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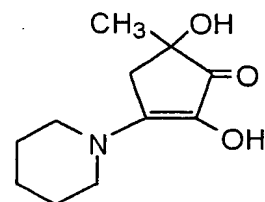
F-16



F-17



F-18



F-19

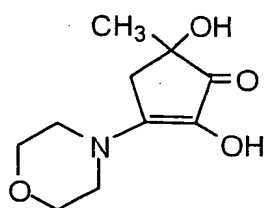


Table 3  
Construction of 14th layer (High-speed blue sensitive layer)

Sample	Emulsion	H.B.S.	Surfactant	Coupler	Remarks
101	Em-A1	HBS-1	W-4	ExY-6	Comp.
102	Em-A2	HBS-1	W-4	ExY-6	Comp.
103	Em-A2	S-1	A-1	ExY-6	Inv.
104	Em-A2	S-37	A-1	ExY-6	Inv.
105	Em-A2	HBS-1	W-4	II-12	Inv.
106	Em-A2	HBS-1	W-4	II-106	Inv.
107	Em-A2	HBS-1	W-4	II-12, II-106	Inv.
108	Em-A2	S-1	A-1	II-12, II-106	Inv.
109	Em-A3	S-1	A-1	II-12, II-106	Inv.
110	Em-A4	HBS-1	W-4	ExY-6	Comp.
111	Em-A5	HBS-1	W-4	ExY-6	Comp.
112	Em-A5	S-1	A-1	II-12, II-106	Inv.
113	Em-A6	S-1	A-1	II-12, II-106	Inv.
114	Em-A7	HBS-1	W-4	ExY-6	Comp.
115	Em-A8	HBS-1	W-4	ExY-6	Comp.
116	Em-A8	S-1	A-1	II-12, II-106	Inv.
117	Em-A9	S-1	A-1	II-12, II-106	Inv.
118	Em-A10	HBS-1	W-4	ExY-6	Comp.
119	Em-A11	HBS-1	W-4	ExY-6	Comp.
120	Em-A11	S-1	A-1	II-12, II-106	Inv.
121	Em-A12	S-1	A-1	II-12, II-106	Inv.
122	Em-A13	HBS-1	W-4	ExY-6	Comp.
123	Em-A14	HBS-1	W-4	ExY-6	Comp.
124	Em-A14	S-1	A-1	II-12, II-106	Inv.
125	Em-A15	S-1	A-1	II-12, II-106	Inv.

H.B.S = High boiling organic solvent

Table 4  
Construction of 11th layer (High-speed green sensitive layer)

Sample	Emulsion	H.B.S.	Surfactant	Coupler	Remarks
201	Em-P1	HBS-1	W-4	EXY-5	Comp.
202	Em-P2	HBS-1	W-4	EXY-5	Comp.
203	Em-P2	S-1	A-1	II-12, II-106	Inv.
204	Em-P3	S-1	A-1	II-12, II-106	Inv.
205	Em-P4	HBS-1	W-4	EXY-5	Comp.
206	Em-P5	HBS-1	W-4	EXY-5	Comp.
207	Em-P5	S-1	A-1	II-12, II-106	Inv.
208	Em-P6	S-1	A-1	II-12, II-106	Inv.
209	Em-P7	HBS-1	W-4	EXY-5	Comp.
210	Em-P8	HBS-1	W-4	EXY-5	Comp.
211	Em-P8	S-1	A-1	II-12, II-106	Inv.
212	Em-P9	S-1	A-1	II-12, II-106	Inv.
213	Em-P10	HBS-1	W-4	EXY-5	Comp.
214	Em-P11	HBS-1	W-4	EXY-5	Comp.
215	Em-P11	S-1	A-1	II-12, II-106	Inv.
216	Em-P12	S-1	A-1	II-12, II-106	Inv.

H.B.S = High boiling organic solvent



Table 5  
Construction of 6th layer (High-speed red sensitive layer)

Sample	Emulsion	H.B.S.	Surfactant	Coupler	Remarks
301	Em-J1	HBS-1	W-4	ExC-6	Comp.
302	Em-J2	HBS-1	W-4	ExC-6	Comp.
303	Em-J2	S-1	A-1	II-12, II-106	Inv.
304	Em-J3	S-1	A-1	II-12, II-106	Inv.
305	Em-J4	HBS-1	W-4	ExC-6	Comp.
306	Em-J5	HBS-1	W-4	ExC-6	Comp.
307	Em-J6	HBS-1	W-4	ExC-6	Comp.
308	Em-J7	HBS-1	W-4	ExC-6	Comp.
309	Em-J8	HBS-1	W-4	ExC-6	Comp.
310	Em-J9	HBS-1	W-4	ExC-6	Inv.
311	Em-J10	HBS-1	W-4	ExC-6	Inv.
312	Em-J11	HBS-1	W-4	ExC-6	Inv.
313	Em-J12	HBS-1	W-4	ExC-6	Inv.
314	Em-J13	HBS-1	W-4	ExC-6	Inv.
315	Em-J11	S-1	A-1	II-12, II-106	Inv.
316	Em-J14	HBS-1	W-4	ExC-6	Comp.
317	Em-J15	HBS-1	W-4	ExC-6	Comp.
318	Em-J16	HBS-1	W-4	ExC-6	Inv.
319	Em-J16	S-1	A-1	II-12, II-106	Inv.
320	Em-J17	S-1	A-1	II-12, II-106	Inv.
321	Em-J18	HBS-1	W-4	ExC-6	Comp.
322	Em-J19	HBS-1	W-4	ExC-6	Comp.
323	Em-J20	HBS-1	W-4	ExC-6	Inv.
324	Em-J20	S-1	A-1	II-12, II-106	Inv.
325	Em-J21	S-1	A-1	II-12, II-106	Inv.
326	Em-J22	HBS-1	W-4	ExC-6	Comp.
327	Em-J23	HBS-1	W-4	ExC-6	Comp.
328	Em-J24	HBS-1	W-4	ExC-6	Inv.
329	Em-J24	S-1	A-1	II-12, II-106	Inv.
330	Em-J25	S-1	A-1	II-12, II-106	Inv.

H.B.S = High boiling organic solvent

Evaluations of the samples are as follows. The samples were subjected to light for 1/100 sec through continuous wedges and a gelatin filter SC-39, which is a long wavelength light transmitting filter having a cut-off wavelength of 390nm, manufactured by Fuji Photo Film Co., Ltd. The development was carried out by the use of automatic processor FP-360B manufactured by Fuji Photo Film Co., Ltd. under the following conditions. The apparatus was reworked so as to prevent the flow of overflow solution from the bleaching bath toward subsequent baths and to, instead, discharge all the solution into a waste solution tank. This FP-360B is fitted with an evaporation correcting means described in JIII Journal of Technical Disclosure No. 94-4992 issued by Japan Institute of Invention and Innovation.

The processing steps and compositions of processing solutions are as follows.

(Processing steps)

Step	Time	Temp.	Qty. of re-plenisher*	Tank vol.
Color development	3 min 5 sec	37.8°C	20 mL	11.5 L
Bleaching	50 sec	38.0°C	5 mL	5 L
Fixing (1)	50 sec	38.0°C	-	5 L
Fixing (2)	50 sec	38.0°C	8 mL	5 L
Washing	30 sec	38.0°C	17 mL	3 L
Stabilization (1)	20 sec	38.0°C	-	3 L
Stabilization (2)	20 sec	38.0°C	15 mL	3 L

ation (2)

Drying                      1 min      60°C  
                             30 sec

5

\* The replenishment rate is a value per 1.1 m of a 35-mm wide lightsensitive material (equivalent to one 24 Ex. film).

10

The stabilizer was fed from stabilization (2) to stabilization (1) by counter current, and the fixer was also fed from fixing (2) to fixing (1) by counter current. All the overflow of washing water was

15

introduced into fixing bath (2). The amounts of drag-in of developer into the bleaching step, drag-in of bleaching solution into the fixing step and drag-in of fixer into the washing step were 2.5 mL, 2.0 mL and 2.0 mL, respectively, per 1.1 m of a 35-mm wide lightsensitive material. Each crossover time was 6

20

sec, which was included in the processing time of the previous step.

25

The open area of the above processor was 100 cm<sup>2</sup> for the color developer, 120 cm<sup>2</sup> for the bleaching solution and about 100 cm<sup>2</sup> for the other processing solutions.

The composition of each of the processing solutions was as follows.

30

(Color developer)	Tank soln. (g)	Replenisher (g)
Diethylenetriamine-	3.0	3.0
pentaacetic acid		
Disodium catechol-3,5-	0.3	0.3
disulfonate		
Sodium sulfite	3.9	5.3

35

	Potassium carbonate	39.0	39.0
5	Disodium-N,N-bis(2-sulfo- natoethyl)hydroxylamine	1.5	2.0
	Potassium bromide	1.3	0.3
10	Potassium iodide	1.3 mg	-
	4-Hydroxy-6-methyl-1,3,3a,7- tetrazaindene	0.05	-
15	Hydroxylamine sulfate	2.4	3.3
	2-Methyl-4-[N-ethyl-N- (□-hydroxyethyl)amino]- aniline sulfate	4.5	6.5
20	Water	q.s. ad 1.0 L	
	pH	10.05	10.18

25 This pH was adjusted by the use of potassium  
hydroxide and sulfuric acid.

	(Bleaching soln.)	Tank soln. (g)	Replenisher (g)
30	Fe(III) ammonium 1,3-diamino- propanetetraacetate monohydrate	113	170
35	Ammonium bromide	70	105
	Ammonium nitrate	14	21
40	Succinic acid	34	51
	Maleic acid	28	42
	Water	q.s. ad 1.0 L	
45	pH	4.6	4.0

This pH was adjusted by the use of aqueous  
ammonia.

50 (Fixing (1) tank soln.)

5:95 (by volume) mixture of the above bleaching

tank soln. and the following fixing tank soln, pH 6.8.

	(Fixing (2))	Tank soln. (g)	Replenisher (g)
5	Aq. soln. of ammonium thiosulfate (750 g/L)	240 mL	720 mL
	Imidazole	7	21
10	Ammonium methanethiosulfonate	5	15
	Ammonium methanesulfinat	10	30
15	Ethylenediaminetetraacetic acid	13	39
	Water	q.s. ad 1.0 L	
20	pH	7.4	7.45

This pH was adjusted by the use of aqueous ammonia and acetic acid.

25 (Washing water)

Tap water was passed through a mixed-bed column filled with H-type strongly acidic cation exchange resin (Amberlite IR-120B produced by Rohm & Haas Co.) and OH-type strongly basic anion exchange resin

30 (Amberlite IR-400 produced by the same maker) so as to set the concentration of calcium and magnesium ions at 3 mg/L or less. Subsequently, 20 mg/L of sodium dichloroisocyanurate and 150 mg/L of sodium sulfate were added. The pH of the solution ranged from 6.5 to 7.5.

	(Stabilizer): common to tank solution and replenisher.	(g)
40	Sodium p-toluenesulfinate	0.03
	Polyoxyethylene p-monononylphenyl ether (average polymerization degree 10)	0.2

	Sodium salt of 1,2-benzothiazolin-3-one	0.10
5	Disodium ethylenediaminetetraacetate	0.05
	1,2,4-triazole	1.3
	1,4-bis(1,2,4-triazol-1-ylmethyl)-piperazine	0.75
10	Water	q.s. ad 1.0 L
	pH	8.5

15           The above-mentioned processing was performed to samples 101 to 125. In addition, another set of samples 101 to 125 were left to stand for 3 days under the condition of 50°C and 80%RH, and subjected to the same processing. Evaluations of photographic  
20 performances were conducted by measuring density of the processed samples through a blue filter. Results obtained are set forth in Table 6.

          As set forth in Table 6, the combination of the compound represented by general formula (I) of the  
25 invention with the compound represented by general formula (II) or (III) of the invention; the combination of the compound represented by general formula (I) of the invention with the surfactant of the invention and the high-boiling point organic solvent of the  
30 invention; and the combination of the compound represented by general formula (I) with the compound represented by general formula (IV) or (V) of the invention, attained low fogging and high-speed photographic materials. In addition, the combination

of the compounds represented by formulas (VI) to (X) set forth above, attained photographic materials with strong resistance to fogging during storage.

Table 6

Sample	Photographic performance with blue filter		Photographic performance after subjecting to thermal condition		Remarks
	Sensi-tivity	Fog	Sensi-tivity	Fog	
101	100	0.25	90	0.40	Comp.
102	135	0.35	75	0.75	Comp.
103	135	0.27	120	0.55	Inv.
104	135	0.28	120	0.56	Inv.
105	135	0.28	120	0.56	Inv.
106	135	0.27	120	0.55	Inv.
107	135	0.27	120	0.55	Inv.
108	135	0.26	120	0.55	Inv.
109	137	0.25	128	0.35	Inv.
110	103	0.25	88	0.38	Comp.
111	137	0.36	77	0.78	Comp.
112	137	0.27	121	0.53	Inv.
113	138	0.26	127	0.34	Inv.
114	105	0.26	91	0.39	Comp.
115	139	0.37	83	0.80	Comp.
116	139	0.27	124	0.55	Inv.
117	139	0.26	130	0.33	Inv.
118	99	0.28	88	0.41	Comp.
119	134	0.40	80	0.88	Comp.
120	134	0.29	120	0.56	Inv.
121	135	0.28	128	0.36	Inv.
122	104	0.25	92	0.39	Comp.
123	138	0.36	81	0.79	Comp.
124	138	0.26	121	0.54	Inv.
125	139	0.26	129	0.32	Inv.

The above-mentioned processing was performed to samples 201 to 216. In addition, another set of



samples 201 to 216 were left to stand for 3 days under the condition of 50°C and 80%RH, and subjected to the same processing. Evaluations of photographic performances were conducted by measuring density of the processed samples through a green filter. Results obtained are set forth in Table 7.

As set forth in Table 7, the combination of the compound represented by general formula (I) of the invention with the compound represented by general formula (II) or (III) of the invention; the combination of the compound represented by general formula (I) of the invention with the surfactant of the invention and the high-boiling point organic solvent of the invention; and the combination of the compound represented by general formula (I) with the compound represented by general formula (IV) or (V) of the invention, attained low fogging and high-speed photographic materials. In addition, the combination of the compounds represented by formulas (VI) to (X) set forth above, attained photographic materials with strong resistance to fogging during storage.

Table 7

Sample	Photographic performance with green filter		Photographic performance after subjecting to thermal condition		Remarks
	Sensi-tivity	Fog	Sensi-tivity	Fog	
201	100	0.27	85	0.40	Comp.
202	156	0.40	70	1.05	Comp.
203	155	0.29	125	0.65	Inv.
204	155	0.29	135	0.45	Inv.
205	103	0.26	86	0.40	Comp.
206	158	0.39	72	1.10	Comp.
207	158	0.29	125	0.63	Inv.
208	157	0.29	136	0.43	Inv.
209	99	0.29	83	0.46	Comp.
210	154	0.41	73	1.08	Comp.
211	154	0.31	124	0.65	Inv.
212	155	0.30	133	0.44	Inv.
213	105	0.28	87	0.47	Comp.
214	160	0.40	79	1.11	Comp.
215	159	0.29	127	0.66	Inv.
216	159	0.28	139	0.46	Inv.

The above-mentioned processing was performed to samples 301 to 330. In addition, another set of samples 201 to 216 were left to stand for 3 days under the condition of 50°C and 80%RH, and subjected to the same processing. Evaluations of photographic performances were conducted by measuring density of the processed samples through a red filter. Results obtained are set forth in Table 8.

As set forth in Table 8, the combination of the compound represented by general formula (I) of the

invention with the compound represented by general formula (II) or (III) of the invention; the combination of the compound represented by general formula (I) of the invention with the surfactant of the invention and  
5 the high-boiling point organic solvent of the invention; and the combination of the compound represented by general formula (I) with the compound represented by general formula (IV) or (V) of the invention, attained low fogging and high-speed  
10 photographic materials. In addition, the combination of the compounds represented by formulas (VI) to (X) set forth above, attained photographic materials with strong resistance to fogging during storage.

Table 8

Sample	Photographic performance with red filter		Photographic performance after subjecting to thermal condition		Remarks
	Sensi-tivity	Fog	Sensi-tivity	Fog	
301	100	0.27	87	0.42	Comp.
302	158	0.41	76	1.20	Comp.
303	158	0.29	103	0.81	Inv.
304	159	0.29	125	0.50	Inv.
305	118	0.28	98	0.43	Comp.
306	125	0.27	105	0.41	Comp.
307	128	0.26	107	0.40	Comp.
308	124	0.25	103	0.40	Comp.
309	116	0.26	95	0.41	Comp.
310	172	0.41	92	1.18	Inv.
311	178	0.40	94	1.18	Inv.
312	180	0.42	96	1.20	Inv.
313	176	0.41	93	1.20	Inv.
314	169	0.40	85	1.19	Inv.
315	177	0.27	111	0.78	Inv.
316	103	0.28	88	0.43	Comp.
317	160	0.40	78	1.18	Comp.
318	178	0.40	83	1.19	Inv.
319	177	0.29	112	0.82	Inv.
320	177	0.28	141	0.48	Inv.
321	99	0.30	86	0.44	Comp.
322	158	0.42	74	1.25	Comp.
323	175	0.41	92	1.21	Inv.
324	176	0.31	111	0.84	Inv.
325	177	0.31	142	0.49	Inv.
326	105	0.28	88	0.42	Comp.
327	163	0.40	78	1.20	Comp.
328	181	0.40	93	1.20	Inv.
329	180	0.29	113	0.85	Inv.
330	181	0.28	144	0.45	Inv.

The results set forth above reveal that the combination of the compounds of the invention can attain silver halide photographic materials having high speed, and low fogging, and low sensitivity decrease and low fog increase due to storage under thermal conditions.

(Example 2)

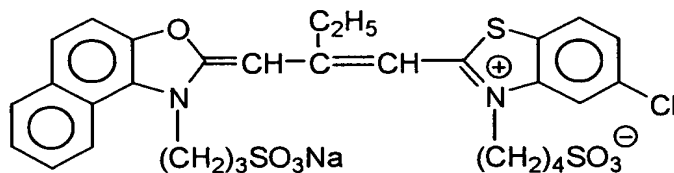
Emulsion Em-X1: (100) silver iodobromide tabular emulsion

A polyvinyl alcohol (having vinyl acetate with polymerization degree of 1700, and average saponification rate of 98% in alcohol, hereinafter referred to as polymer (PV)) and an aqueous gelatin solution (1200mL of water containing 5g of a polymer (PV) and 8g of a deionized alkali-processed gelatin) were prepared in a reaction vessel. The pH was adjusted to 11 and the temperature was held at 55°C. While the resultant solution was stirred, 200mL of Ag-1 solution (containing 0.58 mol/L of  $\text{AgNO}_3$ ) and 200mL of X-1 solution (containing 0.58 mol/L of KBr) were added over 40 minutes. The addition was performed by the double-jet method using a precision liquid transmission pump.

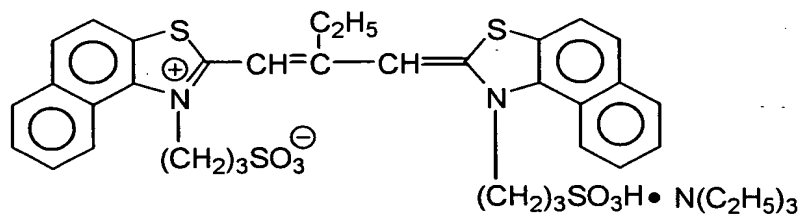
After 5 minutes had passed, the pH was adjusted to 6. An Ag-2 solution (containing 1.177 mol/L of  $\text{AgNO}_3$ ) and a X-2 solution (containing 1.177 mol/L of KBr) were used. While the pBr was maintained at 3.1, 600mL of

each solution was added at a flow rate of 12mL/minute by the fixed quantity double-jet method. Then, an aqueous gelatin solution (200mL of water containing 30g of gelatin) and the spectral sensitizing dyes 22, 23 and 24 were added, 100mL of each of the Ag-3 solution (2.94 mol/L of AgNO<sub>3</sub>) and X-3 solution (2.7 mol/L of KBr, 0.24 mol/L of KI) were added at 5mL/minute. The grain formation step was completed. Thereafter, the temperature was raised to 35°C, and washed with water by a precipitation washing method. A gelatin solution was added to redisperse the emulsion, and the pH and the pAg were adjusted to 6 and 8.7, respectively.

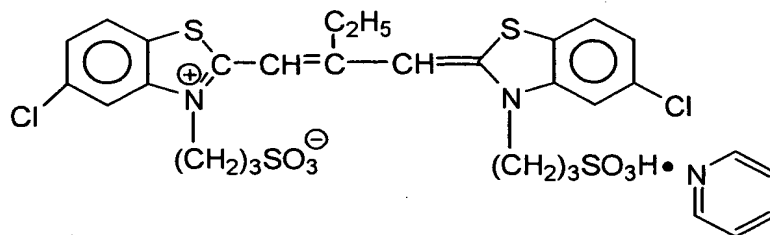
Sensitizing dye 22



Sensitizing dye 23



Sensitizing dye 24



The grains thus prepared are occupied by the

following grains in an amount of 93% or more of the total projected area, which was obtained from replica TEM images of emulsion grains: main planes are (100) planes, an equivalent-circle diameter is  $0.4\mu\text{m}$  or more, a thickness is  $0.08\mu\text{m}$ , and an aspect ratio is 9.5 or more.

The above emulsion was optimally chemically sensitized referring to Em-J1 of Example 1, except for the sensitizing dyes.

10 (Em-X2)

Em-X2 was obtained in the same manner as Em-X1, except that compound (I-13) of the invention was added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time of chemical sensitization.

15 (Em-X3)

Em-X3 was obtained in the same manner as Em-X1, except that compound (IV-2) of the invention was added at the time of chemical sensitization in an amount of 10 mol% of the sensitizing dyes added.

20 (Em-X4)

Em-X4 was obtained in the same manner as Em-X3, except that compound (IX-2-50) of the invention was added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time of chemical sensitization.

25 Each emulsion in a dissolved state was left to stand for 30 min at  $40^{\circ}\text{C}$ . On a cellulose triacetate film support provided with an under coat layer, each of

the above emulsions Em-X1 to -X4 was coated with the coating conditions set forth in Table 9 below.

Table 9

5	(1) Emulsion layer
	Emulsion: Each emulsion (silver $1.63 \times 10^{-2} \text{ mol/m}^2$ )
	Coupler
	ExM-1 ( $2.26 \times 10^{-3} \text{ mol/m}^2$ )
10	ExY-5 ( $8.0 \times 10^{-3} \text{ g/m}^2$ )
	High boiling organic solvent ( $1.8 \times 10^{-1} \text{ g/m}^2$ )
	Gelatin ( $3.24 \text{ g/m}^2$ )
	Surfactant
15	(2) Protective layer
	H-1 ( $0.08 \text{ g/m}^2$ )
	Gelatin ( $1.8 \text{ g/m}^2$ )

20 Samples 401 to 405 were prepared by replacing the emulsion to be coated, as set forth in Table 10.

Table 10

Sample	Emulsion	H.B.S.	Surfactant	Coupler (with respect to ExY-5)	Remarks
401	Em-X1	HBS-1	W-4	ExY-5	Comp.
402	Em-X2	HBS-1	W-4	ExY-5	Comp.
403	Em-X2	S-1	A-1	II-12, II-106	Inv.
404	Em-X3	S-1	A-1	II-12, II-106	Inv.
405	Em-X4	S-1	A-1	II-12, II-106	Inv.

H.B.S. = High oiling organic solvent

These samples were subjected to hardening



processing at 40°C, relative humidity of 70% for 14 hr. Thereafter, the samples were exposed to light for 1/100 sec through continuous wedges, and subjected to the development processing below. Density of the processed samples was measured with a green filter to obtain photographic speed and fog density before the long-term storage. Sensitivity was indicated in a relative value of a reciprocal of an exposure amount required to reach the density of fog density plus 0.2. As an evaluation of storage fogging of the sensitive materials, the samples were stored for 14 days under the conditions of 40°C and relative humidity of 60%. Then, the samples were exposed to light for 1/100 sec, and subjected to the development processing below. Density of the processed samples was measured with a green filter to obtain fog density after the long-term storage. The density difference between before and after storage was calculated.

The processing was carried out by the use of automatic processor FP-362B manufactured by Fuji Photo Film Co., Ltd.

The processing steps and compositions of processing solutions are as follows.

(Processing steps)

Step	Time	Temp.	Qty. of re-plenisher*	Tank vol.
Color development	3 min 5 sec	38.0°C	15 mL	10.3 L

	Bleaching	50 sec	38°C	5 mL	3.6 L
	Fixing (1)	50 sec	38°C	-	3.6 L
5	Fixing (2)	50 sec	38°C	7.5 mL	3.6 L
	Stabilization (1)	20 sec	38°C	-	1.9 L
10	Stabilization (2)	20 sec	38°C	-	1.9 L
	Stabilization (3)	20 sec	38°C	30 mL	1.9 L
15	Drying	1 min 30 sec	60°C		

20 \* The replenishment rate is a value per 1.1 m of a 35-mm wide lightsensitive material (equivalent to one 24 Ex. film).

25 The stabilizer was counterflowed in the order of (3) → (2) → (1), and the fixer was also connected from (2) to (1) by counterflow piping. Also, the tank solution of stabilizer (2) was supplied to fixer (2) in an amount of 15 mL as a replenishment rate.

30 Additionally, as the developer a color developer (A) replenisher and a color developer (B) replenisher having the following compositions were replenished in amounts of 12 mL and 3 mL, respectively, i.e., a total of 15 mL, as a replenishment rate. Note that the amounts of the developer, bleaching solution, and fixer carried over to the bleaching step, fixing step, and

35 washing step, respectively, were 2.0 mL per 1.1m of a 35-mm wide sensitized material. Note also that each crossover time was 6 sec, and this time was included in the processing time of each preceding step.

The compositions of the processing solutions are presented below.

5	(Color developer (A))	[Tank solution]	
	[Replenisher]		
	Diethylenetriamine	2.0g	4.0g
	pentaacetic acid		
10	Sodium 4,5-dihydroxy	0.4g	0.5g
	benzene-1,3-disulfonate		
15	Disodium-N,N-bis(2-	10.0g	15.0g
	sulfonateethyl)		
	hydroxylamine		
	Sodium sulfite	4.0g	9.0g
	Hydroxylamine sulfate	2.0g	-
20	Potassium bromide	1.4g	-
	Diethyleneglycol	10.0g	17.0g
25	Ethyleneurea	3.0g	5.5g
	2-methyl-4-[N-ethyl-N-	4.7g	11.4g
	( $\beta$ -hydroxyethyl)amino]		
	aniline sulfate		
30	Potassium carbonate	39g	59g
	Water to make	1.0L	1.0L
35	pH (controlled by sulfuric acid and KOH)	10.05	10.50

The above tank solution indicates the composition after (color developer (B)) below was mixed.

40	(Color developer (B))	[Tank solution]	
	[Replenisher]		
	Hydroxylamine sulfate	2.0g	4.0g
45	Water to make	1.0L	1.0L
	pH (controlled by sulfuric acid and KOH)	10.05	4.0

50 The above tank solution indicates the composition after (color developer (A)) described above was mixed.

	(Bleaching solution) [Replenisher]	[Tank solution]	
5	Ferric ammonium 1,3- diaminopropanetetra acetate monohydrate	120g	180g
	Ammonium bromide	50g	70g
10	Succinic acid	30g	50g
	Maleic acid	40g	60g
	Imidazole	20g	30g
15	Water to make	1.0L	1.0L
	pH (controlled by ammonia water and nitric acid)	4.6	4.0
20	(Fixer) [Replenisher]	[Tank solution]	
25	Ammonium thiosulfate (750 g/L)	280 mL	1,000 mL
	Aqueous ammonium bisulfite solution (72%)	20g	80g
30	Imidazole	5g	45g
	1-mercapto-2-(N,N- dimethylaminoethyl)- tetrazole	1g	3g
35	Ethylenediamine tetraacetic acid	8g	12g
	Water to make	1L	1L
40	pH (controlled by ammonia water and nitric acid)	7.0	7.0
45	(Stabilizer) [Common to tank solution and replenisher]		
	Sodium p-toluenesulfinate		0.03g
	p-Nonylphenoxypolyglycidol (glycidol average polymerization degree 10)		0.4g
50	Disodium ethylenediaminetetraacetate		0.05g
55	1,2,4-triazole		1.3g

	1,4-bis(1,2,4-triazole-1-isomethyl) piperazine	0.75g
5	1,2-benzisothiazoline-3-one	0.10g
	Water to make	1.0L
	pH	8.5

The results of the evaluations are set forth in Table 11. Sensitivity is indicated in a relative value of a reciprocal of an exposure amount required to reach a fog density plus 0.2. In the emulsion of the present invention, the combination of the compound represented by general formula (I) of the invention with the compound represented by general formula (II) or (III) of the invention; the combination of the compound represented by general formula (I) of the invention with the surfactant of the invention and the high-boiling point organic solvent of the invention; and the combination of the compound represented by general formula (I) with the compound represented by general formula (IV) of the invention, attained low fogging and high-speed photographic materials. In addition, the combination of the compounds represented by formulas (VI) to (X) set forth above, attained photographic materials with strong resistance to fogging during storage.

Table 11

Sample	Sensi- tivity	Fog	Sensitivity after subjecting to thermal condition	Fog after subjecting to thermal condition	Remarks
401	100	0.25	84	0.42	Comp.
402	145	0.45	65	1.1	Comp.
403	144	0.26	127	0.64	Inv.
404	145	0.24	133	0.43	Inv.
405	152	0.23	135	0.44	Inv.

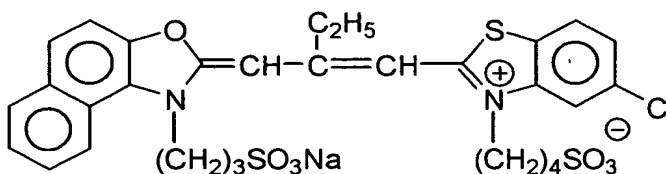
(Example 3)

Emulsion Em-Y1: (111) silver chloride tabular  
5 emulsion

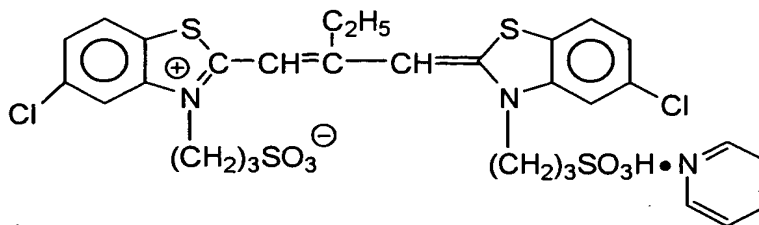
Into 1.2L of water, 2.0g of sodium chloride and  
2.8g of an inert gelatin were added, 60mL of Ag-1  
solution (containing 9g of AgNO<sub>3</sub>) and 60mL of X-1  
solution (containing 3.2g of sodium chloride) were  
10 added by the double jet method over 1 minute while  
maintaining the temperature in the vessel at 35°C. One  
minute after the completion of the addition, 0.8  
millimole of N-benzyl-4-phenylpyridinium chloride was  
added. Additional 1 min after that, 3.0g of sodium  
15 chloride was added. The temperature in the reaction  
vessel was raised to 60°C over the next 25 min. After  
ripening the mixture for 16 min at 60°C, 560g of 10%  
phthalated gelatin aqueous solution and  $1 \times 10^{-5}$  mole  
of sodium thiosulfonate were added. Thereafter,  
20 317.5mL of Ag-2 solution (containing 127g of AgNO<sub>3</sub>), X-  
2 solution (containing 54.1g of sodium chloride), and

160mL of crystal habit-controlling agent 1 solution (M/50) were added over 20 min at accelerated flow rates. Additional 2 min after that, Ag-3 solution (containing 34g of AgNO<sub>3</sub>) and X-3 solution (containing 11.6g of sodium chloride and 1.27 mg of yellow prussiate of potash) were added over 5 min. Then, 33.5mL of 0.1N thiocyanic acid, and 0.32 millimole of sensitizing dye 25, 0.48 millimole of sensitizing dye 26, and 0.05 millimole of sensitizing dye 27 were added.

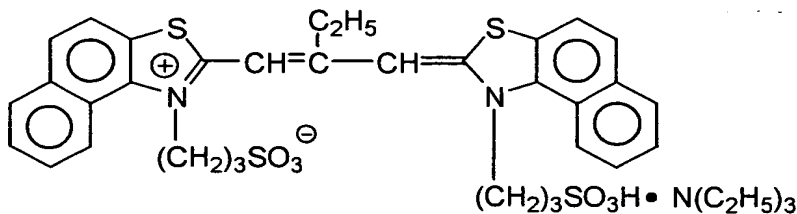
Sensitizing dye 25



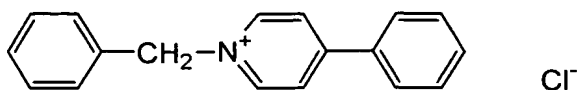
Sensitizing dye 26



Sensitizing dye 27



Crystal habit-controlling agent 1



The temperature was decreased to 40°C, and washed with water by a precipitation washing method. An

aqueous gelatin solution was added to redisperse the emulsion, and the pH and the pAg were adjusted to 6.2 and 7.5, respectively.

5       The grains thus prepared were occupied by the following grains in an amount of 50% or more of the total projected area, which was obtained from replica TEM images of emulsion grains: main planes are (111) planes, an equivalent-sphere diameter is 0.56-0.66  $\mu\text{m}$ , a projected area diameter is 0.95-1.15  $\mu\text{m}$ , and a grain  
10       thickness is 0.12-0.16  $\mu\text{m}$ .

      The above emulsion was optimally chemically sensitized referring to Em-J1 of Example 1, except for the sensitizing dyes to obtain Em-Y1.

      (Em-Y2)

15       Em-Y2 was obtained in the same manner as Em-Y1, except that compound (I-13) of the invention was added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time of chemical sensitization.

      (Em-Y3)

20       Em-Y3 was obtained in the same manner as Em-Y1, except that compound (IV-2) of the invention was added at the time of chemical sensitization in an amount of 10 mol% of the sensitizing dyes added.

      (Em-Y4)

25       Em-Y4 was obtained in the same manner as Em-Y3, except that compound (IX-2-50) of the invention was added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time



of chemical sensitization.

Each emulsion in a dissolved state was left to stand for 30 min at 40°C. On a cellulose triacetate film support provided with an under coat layer, each of the above emulsions Em-Y1 to -Y4 was coated with the coating conditions set forth in Table 9 above.

Samples 501 to 505 were prepared by replacing the emulsion to be coated as set forth in Table 12.

Table 12

Sample	Emulsion	H.B.S.	Surfactant	Coupler (with respect to ExY-5)	Remarks
501	Em-Y1	HBS-1	W-4	ExY-5	Comp.
502	Em-Y2	HBS-1	W-4	ExY-5	Comp.
503	Em-Y2	S-1	A-1	II-12, II-106	Inv.
504	Em-Y3	S-1	A-1	II-12, II-106	Inv.
505	Em-Y4	S-1	A-1	II-12, II-106	Inv.

H.B.S. = High oiling organic solvent

The results of the evaluations conducted in the same manner as in Example 3 are set forth in Table 13 below. Sensitivity is indicated in a relative value of a reciprocal of an exposure amount required to reach a fog density plus 0.2. In the emulsion of the present invention, the combination of the compound represented by general formula (I) of the invention with the compound represented by general formula (II) or (III)

of the invention; the combination of the compound represented by general formula (I) of the invention with the surfactant of the invention and the high-boiling point organic solvent of the invention; and the combination of the compound represented by general formula (I) with the compound represented by general formula (IV) of the invention, attained low fogging and high-speed photographic materials. In addition, the combination of the compounds represented by formulas (VI) to (X) set forth above, attained photographic materials with strong resistance to fogging during storage.

Table 13

Sample	Sensitivity	Fog	Sensitivity after subjecting to thermal condition	Fog after subjecting to thermal condition	Remarks
501	100	0.28	83	0.48	Comp.
502	143	0.48	62	1.2	Comp.
503	141	0.28	125	0.68	Inv.
504	143	0.26	132	0.48	Inv.
505	150	0.27	134	0.49	Inv.

(Example 4)

Emulsion Em-Z1: (100) silver chloride tabular emulsion containing, in a shell portion, 0.4 mol% of iodide with respect to the total silver amount

1200mL of water, 25g of gelatin, 0.4g of sodium chloride, and 4.5mL of 1N silver nitrate solution (pH=4.5) were added into a reaction vessel and

maintained the temperature at 40°C. Next, Ag-1 solution (silver nitrate 0.2g/mL) and X-1 solution (sodium chloride 0.069g/mL) were added at a flow rate of 48mL/min over 4 min while vigorously stirring the mixture. 15 sec after that, 150mL of an aqueous polyvinyl alcohol solution (containing 6.7g of polyvinylalcohol having vinyl acetate with polymerization degree of 1700, and average saponification rate of 98% or more in alcohol, hereinafter referred to as PVA-1 in 1 L of water) was added and pH was adjusted to 3.5. The temperature was raised to 75°C over 15 min, 23mL of 1N aqueous sodium hydroxide solution was added to adjust pH to 6.5. 4.0mL of 1-(5-methylureidophenyl)-5-mercaptotetrazole (0.05%) and 4.0mL of N,N'-dimethylimidazolidine-2-thion (1% aqueous solution) were added.

After adding 4g of sodium chloride, followed by adjustment of the silver potential against a saturated calomel electrode at room temperature to 100mV, the Ag-1 solution and X-1 solution were added over 15 min at a linearly increasing flow rate from 40mL/min to 42mL/min, while maintaining the silver potential at 100mV. In addition, 12.5mL of 1N silver nitrate aqueous solution was added to adjust the pH at 4.0. After 28.8g of sodium chloride was added, followed by adjusting the silver potential at 60mV, 0.38 millimole of sensitizing dye 25, 0.56 millimole of sensitizing dye 26, and 0.06

millimole of sensitizing dye 27, and Ag-2 solution (silver nitrate 0.1g/mL) and X-2 solution (an aqueous solution containing 33.8g of sodium chloride and 1.95g of potassium iodide in 1L, so that the total amount of iodide becomes 0.4 mol% of the total silver amount) was added at a flow rate of 40mL/min. Thereafter, the mixture was left to stand for 10 min at 75°C.

The temperature was decreased to 40°C, and washed with water by a precipitation washing method. An aqueous gelatin solution was added to redisperse the emulsion, and the pH and the pAg were adjusted to 6.0 and 7.3, respectively.

The grains thus prepared were occupied by the following grains in an amount of 50% or more of the total projected area, which was obtained from replica TEM images of emulsion grains: main planes are (100) planes, an equivalent-sphere diameter is 0.4-0.5 $\mu$ m, a grain thickness is 0.10-0.12  $\mu$ m, an aspect ratio is 6.5 or more, and ratio of neighboring sides is 1.1-1.3.

The above emulsion was optimally chemically sensitized referring to Em-J1 of Example 1, except for the sensitizing dyes to obtain Em-Z1.

(Em-Z2)

Em-Z2 was obtained in the same manner as Em-Z1, except that compound (I-13) of the invention was added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time of chemical sensitization.

(Em-Z3)

Em-Z3 was obtained in the same manner as Em-Z1, except that compound (IV-2) of the invention was added at the time of chemical sensitization in an amount of  
5 10 mol% of the sensitizing dyes added.

(Em-Z4)

Em-Z4 was obtained in the same manner as Em-Z3, except that compound (IX-2-50) of the invention was added in an amount of  $1 \times 10^{-4}$  mol/mol Ag at the time  
10 of chemical sensitization.

Each emulsion in a dissolved state was left to stand for 30 min at 40°C. On a cellulose triacetate film support provided with an under coat layer, each of the above emulsions Em-Z1 to -Z4 was coated with the  
15 coating conditions set forth in Table 9 above.

Samples 601 to 605 were prepared by replacing the emulsion to be coated as set forth in Table 14.

Table 14

Sample	Emulsion	H.B.S.	Surfactant	Coupler (with respect to ExY-5)	Remarks
601	Em-Z1	HBS-1	W-4	ExY-5	Comp.
602	Em-Z2	HBS-1	W-4	ExY-5	Comp.
603	Em-Z2	S-1	A-1	II-12, II-106	Inv.
605	Em-Z3	S-1	A-1	II-12, II-106	Inv.
606	Em-Z4	S-1	A-1	II-12, II-106	Inv.

H.B.S. = High oiling organic solvent

5. Evaluation was conducted in the similar manner as in Example 3. The results obtained are set forth below.

Table 15

Sample	Sensi- tivity	Fog	Sensitivity after subjecting to thermal condition	Fog after subjecting to thermal condition	Remarks
601	100	0.30	80	0.47	Comp.
602	145	0.50	65	1.15	Comp.
603	144	0.31	123	0.67	Inv.
604	145	0.30	133	0.45	Inv.
605	152	0.31	135	0.46	Inv.

10 Sensitivity is indicated in a relative value of a reciprocal of an exposure amount required to reach a fog density plus 0.2. In the emulsion of the present invention, the combination of the compound represented by general formula (I) of the invention with the compound represented by general formula (II) or (III) of the invention; the combination of the compound

represented by general formula (I) of the invention with the surfactant of the invention and the high-boiling point organic solvent of the invention; and the combination of the compound represented by general  
5 formula (I) with the compound represented by general formula (IV) of the invention, attained low fogging and high-speed photographic materials. In addition, the combination of the compounds represented by formulas (VI) to (X) set forth above, attained photographic  
10 materials with strong resistance to fogging during storage.

Additional advantages and modifications will readily occur to those skilled in the art. Therefore, the invention in its broader aspects is not limited to  
15 the specific details and representative embodiments shown and described herein. Accordingly, various modifications may be made without departing from the spirit or scope of the general inventive concept as defined by the appended claims and their equivalents.